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Desulfonyloxyiodination of arenesulfonic acids with *m*CPBA and molecular iodine

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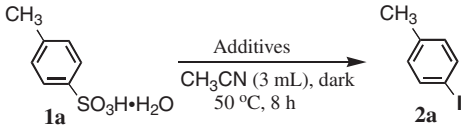
ABSTRACT

Treatment of *p*-alkylbenzenesulfonic acids with *m*CPBA and molecular iodine gave *p*-alkyliodobenzenes in good to moderate yields via electrophilic *ipso*-substitution by the iodonium species (I^+) formed. This desulfonyloxyiodination was promoted by the addition of a catalytic amount of iodoarenes, such as *o*-iodobenzoic acid. The same treatment of dimethylbenzenesulfonic acids and trimethylbenzenesulfonic acids with *m*CPBA and molecular iodine proceeded smoothly both in the absence and in the presence of *o*-iodobenzoic acid to provide the corresponding monoiodo-dimethylbenzene and diiodo-dimethylbenzene, and diiodo-trimethylbenzene and triiodo-trimethylbenzene, in good to moderate yields, respectively. On the other hand, the same desulfonyloxyiodination of benzenesulfonic acid and *p*-chlorobenzenesulfonic acid with *m*CPBA and molecular iodine proceeded only in the presence of *o*-iodobenzoic acid to generate iodobenzene and *p*-chloroiodobenzene, respectively, in moderate yields.

The use of hypervalent iodines in organic synthesis has been widely studied.[1] (Diacetoxyiodo)benzene (DIB) and [(hydroxy)-(tosyloxy)iodo]benzene (HTIB) are the most popular and useful trivalent iodine reagents for organic synthesis because they are good alternatives to toxic heavy-metal oxidants.[2] On the other hand, today, the ArI-catalyzed oxidative conversion reactions of substrates, such as ketones, hydroquinones, and alcohols, with *m*-chloroperbenzoic acid (*m*CPBA) or Oxone® have become very popular[3] because they are metal-free oxidative reactions and thus conform to environmentally benign organic synthesis. Recently, we reported an efficient method for the preparation of various [(hydroxy)(sulfonyloxy)iodo]arenes directly from iodoarenes with *m*CPBA and sulfonic acids at room temperature;[4] the PhI-catalyzed, polymer-supported PhI-catalyzed, and ion-supported PhI-catalyzed α-tosyloxylation of ketones with *m*CPBA and *p*-toluenesulfonic acid monohydrate;[5a–c] the PhI-catalyzed and ion-supported PhI-catalyzed preparation of 3,4-dihydro-1*H*-2,1-benzothiazine 2,2-dioxides from *N*-methoxy-2-arylethanesulfonamides with *m*CPBA;[5d,5e] and the ArI-catalyzed oxazole preparation from ketones and nitriles with *m*CPBA[5f] or Oxone®.[5g]

Herein, as part of our study on the catalytic use of organoiodines (I) in organic synthesis, we would like to report the desulfonyloxyiodination of arenesulfonic acids with *m*CPBA and molecular iodine both in the presence and in the absence of *o*-iodobenzoic acid. First, to an acetonitrile solution of *p*-toluenesulfonic acid monohydrate (1 mmol) were added molecular iodine, molecular iodine/*tert*-BuOOH (~70%), and molecular iodine/H_2O_2–urea, and the reaction mixtures were stirred at 50 °C for 8 h, as shown in Table 1 (entries 1, 3, and 4). However, *p*-iodotoluene was not formed at all. When the same reaction was carried out with molecular iodine/Oxone®, *p*-iodotoluene was obtained in 23% yield (entry 2). Moreover, when *p*-toluenesulfonic acid monohydrate was treated with NIS (*N*-iodosuccinimide) or molecular iodine/*m*CPBA in acetonitrile, *p*-iodotoluene was obtained in moderate yields, as shown in entries 5–8. When *o*-iodobenzoic acid (0.1 equiv or 1.1 equiv) was added to the solution, the yield of *p*-iodotoluene was increased to 75% (entries 9 and 10).[6] On the other hand,

Table 1
Desulfonyloxyiodination of *p*-toluenesulfonic acid



Entry	Additives (equiv)	Yield (%)
1	I_2 (1.2)	0
2	I_2 (1.2), Oxone (1.1)	23
3	I_2 (1.2), ^{t}BuOOH (1.1)	0
4	I_2 (1.2), H_2O_2·urea (1.1)	0
5	NIS (1.1)	58 (33:20[a]:5[b])
6	NIS (1.1), BF_3·Et_2O (2.2)	21
7	I_2 (1.5), *m*CPBA (1.4)	49
8	I_2 (2.0), *m*CPBA (1.1)	45
9	I_2 (1.2), *m*CPBA (1.1), *o*-$HO_2CC_6H_4I$ (0.1)	61
10	I_2 (1.2), *m*CPBA (1.1), *o*-$HO_2CC_6H_4I$ (1.1)	75 (46:22[a]:7[b])

[a] Yield of 1,5-diiodo-2-methylbenzene.
[b] Yield of 1,2-diiodo-4-methylbenzene.

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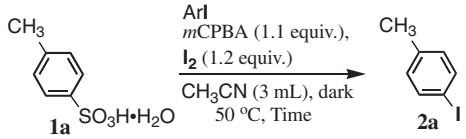
p-bromotoluene was not formed at all, when a solution of *p*-toluenesulfonic acid monohydrate with Br_2 (1.2 equiv)/Oxone® (1.1 equiv), NBS (1.1 equiv), or Br_2 (1.2 equiv)/*m*CPBA (1.1 equiv)/*o*-iodobenzoic acid (1.1 equiv) in acetonitrile was warmed at 50 °C. Thus, the desulfonyloxyiodination of arenesulfonic acids with an oxidant proceeds specifically in the presence of molecular iodine or iodine analogs. In the present desulfonyloxyiodination of *p*-toluenesulfonic acid monohydrate with *m*CPBA (1.1 equiv) and molecular iodine (1.2 equiv) in acetonitrile, the effect of iodoarenes, such as iodobenzene, *p*-iodobenzoic acid, *p*-chloroiodobenzene, *p*-iodotoluene, and *o*-iodobenzoic acid was studied and the results are shown in Table 2. The present desulfonyloxyiodination proceeded smoothly without iodoarene to generate *p*-iodotoluene in 51% yield at 50 °C (entry 1). The addition of iodobenzene (1.1 equiv) promoted the reaction slightly to give *p*-iodotoluene in 60% yield at 50 °C (entry 3), while the same reaction at room temperature was rather slow (entry 2). Entries 5 and 9 indicate that a catalytic amount of iodobenzene and *o*-iodobenzoic acid promoted the present desulfonyloxyiodination. However, the reaction with *o*-iodobenzoic acid is practically convenient, as *o*-iodobenzoic acid can be removed from the reaction mixture by washing with basic aq Na_2SO_3 solution.

Then, *p*-ethylbenzenesulfonic acid, *p*-octylbenzenesulfonic acid, *p*-dodecylbenzenesulfonic acid, and *p*-(β-bromoethyl)benzenesulfonic acid were treated with *m*CPBA and molecular iodine both in the presence and in the absence of a catalytic amount of *o*-iodobenzoic acid (0.1 equiv) in acetonitrile at 50 °C or refluxing conditions to provide *p*-iodoethylbenzene, *p*-iodooctylbenzene, *p*-iododocecylbenzene, and 4-(2′-bromoethyl)-1-iodobenzene, respectively, in moderate to good yields (methods **A** or **B**[6]). In each reaction, the addition of *o*-iodobenzoic acid increased the yield of the desulfonyloxyiodination product in the range of 10–35%, as shown in Table 3 (entries 3–10). Then, under the same conditions, mesitylenesulfonic acid, 2,5-dimethylbenzenesulfonic acid, and 2,4-dimethylbenzenesulfonic acid were treated with *m*CPBA and molecular iodine both in the presence and in the absence of *o*-iodobenzoic acid to generate 1,3-diiodo-2,4,6-trimethylbenzene and 1,3,5-triiodo-2,4,6-trimethylbenzene; 2,5-dimethyl-1-iodobenzene and 1,4-diiodo-2,5-dimethylbenzene; and 2,4-dimethyl-1-iodobenzene and 1,5-diiodo-2,4-dimethylbenzene, respectively, in good yields (entries 11–24). Under acetonitrile refluxing conditions, polyiodoarenes were obtained as major products (entries 14 and 19). The same treatment of 2-iodo-5-methylbenzenesulfonic acid both in the presence and in the absence of *o*-iodobenzoic acid, furnished 1,2-diiodo-4-methylbenzene in good to moderate yields, as shown in entries 25 and 26. In those reactions, *o*-iodobenzoic acid induced the desulfonyloxyiodination to provide iodoarenes in better yields than that in the absence of *o*-iodobenzoic acid. Moreover, when benzenesulfonic acid and *p*-chlorobenzenesulfonic acid were treated with *m*CPBA and molecular iodine under the same conditions without *o*-iodobenzoic acid, the yields of iodobenzene and *p*-chloroiodobenzene were low. However, when the reactions were carried out in the presence of *o*-iodobenzoic acid, iodobenzene, and *p*-chloroiodobenzene were obtained in moderate yields, respectively (entries 27–30). *p*-Methoxybenzenesulfonic acid, which has an electron-rich aromatic group, reacted with molecular iodine and *m*CPBA both in the presence and in the absence of *o*-iodobenzoic acid at room temperature to give 2,4-diiodo-1-methoxybenzene in good yields

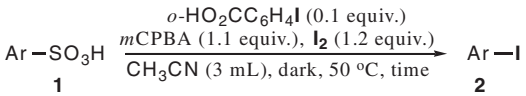
Table 2
Desulfonyloxyiodination of *p*-toluenesulfonic acid

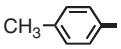
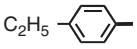
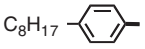
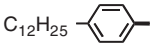
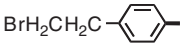
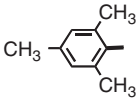
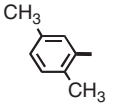
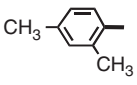
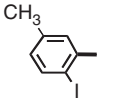
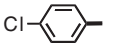
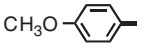
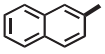
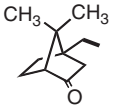


Entry	ArI (equiv)	Time	Yield (%)
1	—	8 h	51
2	Ph**I** (1.1)	16 h[a]	7
3	Ph**I** (1.1)	16 h	60
4	*p*-$HO_2CC_6H_4$**I** (1.1)	8 h	36
5	Ph**I** (0.1)	8 h	60
6	*p*-$HO_2CC_6H_4$**I** (0.1)	8 h	38
7	*p*-ClC_6H_4**I** (0.1)	8 h	44
8	*p*-$H_3CC_6H_4$**I** (0.1)	8 h	36
9	*o*-$HO_2CC_6H_4$**I** (0.1)	8 h	61

[a] Reaction was carried out at rt.

Table 3
Desulfonyloxyiodination of arenesulfonic acids

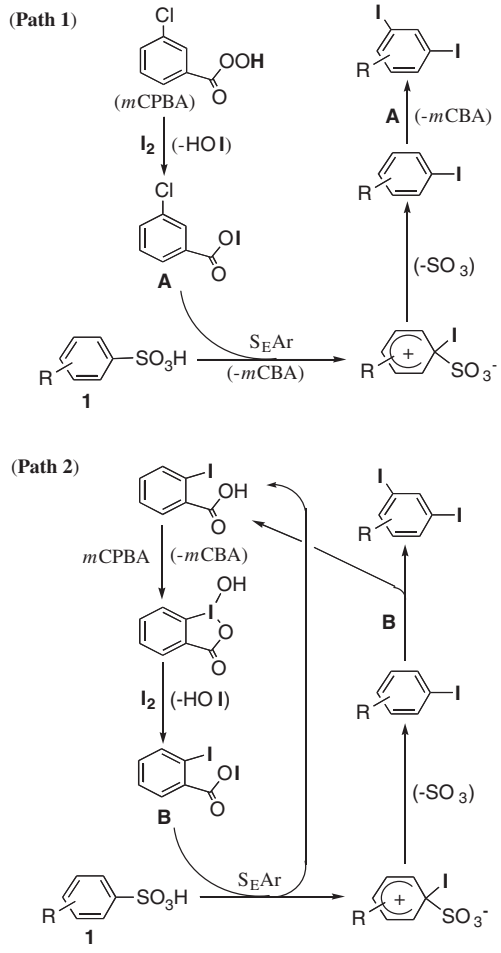


Entry	Ar–	Time	Method	Yield (%)
1		8 h	**A**	61
2		8 h[a]	**A**	51
3		8 h	**A**	63
4		8 h[a]	**A**	43
5		8 h	**B** (reflux)	81
6		8 h[a]	**B** (reflux)	59
7		8 h	**B** (reflux)	88
8		8 h[a]	**B** (reflux)	53
9		8 h	**B** (reflux)	69
10		8 h[a]	**B** (reflux)	62
11		8 h	**A**	76 (58[b]:18[c])
12		63 h[d]	**A**	62 (53[b]:9[c])
13		8 h[a]	**A**	55 (27[b]:28[c])
14		8 h	**A** (reflux)	72 (15[b]:57[c])
15		8 h	**A**	64[e]
16		16 h	**A**	49 (42:7[e])
17		8 h	**A**	78[e]
18		63 h[d]	**A**	68 (53:12[e])
19		8 h	**A** (reflux)	94[e]
20		8 h[a]	**A**	66[e]
21		8 h	**A**	86[f]
22		8 h	**A** (reflux)	96[f]
23		8 h[a]	**A**	76[f]
24		63 h[d]	**A**	70 (38:32[f])
25		8 h	**A** (reflux)	80
26		8 h[a]	**A**	51
27		8 h[g]	**B** (reflux)	40
28		8 h[a]	**B** (reflux)	7
29		8 h[g]	**B** (reflux)	45
30		8 h[a]	**B** (reflux)	5
31		8 h	**A** (rt)	67[h]
32		8 h[a]	**A** (reflux)	69 (47[h]:22[i])
33		8 h[a]	**A** (rt)	67[h]
34		8 h	**A**	65
35		8 h[a]	**A**	62
36		8 h	**A**	0
37		8 h[a]	**A**	0
38		8 h	**A**	0

Methods **A** and **B**: see to experimental procedure (Ref. 6).
[a] Without *o*-$HO_2CC_6H_4I$.
[b] Yield of 1,3-diiodo-2,4,6-trimethylbenzene.
[c] Yield of 1,3,5-triiodo-2,4,6-trimethylbenzene.
[d] Solvent (30 mL) was used.
[e] Yield of 1,4-diiodo-2,5-dimethylbenzene.
[f] Yield of 1,5-diiodo-2,4-dimethylbenzene.
[g] *o*-$HO_2CC_6H_4I$ (1.1 equiv) was used.
[h] Yield of 2,4-diiodo-1-methoxybenzene.
[i] Yield of 2,4,6-triiodo-1-methoxybenzene.

(entries 31 and 33). When the same reaction was carried out under acetonitrile refluxing conditions, a mixture of 2,4-diiodo-1-methoxybenzene and 2,4,6-triiodo-1-methoxybenzene was obtained (entry 32). The same treatment of 1-naphthalenesulfonic acid gave 1-iodonaphthalene in good yields both in the presence and in the absence of *o*-iodobenzoic acid (entries 34 and 35), while 2-iodonaphthalene was not formed at all from the reaction with 2-naphthalenesulfonic acid (entries 36 and 37). This result is closely related to that 1-naphthalenesulfonic acid which is a kinetically controlled product and is isomerized to 2-naphthalenesulfonic acid, a thermodynamically stable product, at high temperature. The desulfonyoxyiodination of 3-nitrobenzenesulfonic acid and 2,4-dinitrobenzenesulfonic acid with *m*CPBA and molecular iodine both in the presence and in the absence of *o*-iodobenzoic acid did not occur at all, as the electrophilic *ipso*-substitution of 3-nitrobenzenesulfonic acid and 2,4-dinitrobenzenesulfonic acid (S_EAr) did not proceed due to their low electron density on the aromatics. Aliphatic sulfonic acids, such as camphorsulfonic acid, also did not react with molecular iodine and *m*CPBA both in the presence and in the absence of *o*-iodobenzoic acid (entry 38). Thus, the present desulfonyloxyiodination reaction with molecular iodine and *m*CPBA both in the presence and in the absence of *o*-iodobenzoic acid occurs only in arenesulfonic acids, particularly those bearing electron-rich aromatic groups.

When toluene was treated with I_2 (1.2 equiv)/*m*CPBA (1.1 equiv)/*o*-iodobenzoic acid (0.1 equiv) in acetonitrile at 50 °C for 8 h under the same conditions, a mixture of *p*-iodotoluene and *o*-iodotoluene was obtained only in 2% yield. Moreover, when *p*-iodotoluene was treated with I_2 (1.2 equiv)/*m*CPBA (1.1 equiv)/*o*-iodobenzoic acid (0.1 equiv) in acetonitrile at 50 °C for 8 h under the same conditions, *p*-iodotoluene was recovered in high yield and 1,2-diiodo-4-methylbenzene was not formed at all. Based on these results and entries 25 and 26, we believe the present reaction proceeds through the reaction mechanism, shown in Scheme 1.[7] In the absence of *o*-iodobenzoic acid, the desulfonyloxyiodination proceeds through path 1. *m*-Chlorobenzoyl hypoiodite **A** reacts with arenesulfonic acids **1** to generate iodoarenes via electrophilic *ipso*-substitution by the iodonium species. On the other hand, the desulfonyloxyiodination of arenesulfonic acids **1** with *m*CPBA and molecular iodine in the presence of *o*-iodobenzoic acid proceeds through both path 1 and path 2. Thus, both *m*-chlorobenzoyl hypoiodite **A** and *o*-iodobenzoyl hypoiodite **B** react with arenesulfonic acids **1** to give iodoarenes, and further electrophilic iodination of the formed iodoarenes with both *m*-chlorobenzoyl hypoiodite **A** and *o*-iodobenzoyl hypoiodite **B** occurs to provide polyiodoarenes, depending on the electron density of the iodoarenes formed.



Scheme 1. Plausible reaction mechanisms.

In conclusion, treatment of *p*-alkylbenzenesulfonic acids with *m*CPBA and molecular iodine gave *p*-alkyliodobenzenes in good to moderate yields via electrophilic *ipso*-substitution by the iodonium species. This desulfonyloxyiodination was promoted by the addition of a catalytic amount of iodoarenes, such as *o*-iodobenzoic acid. Further synthetic study of the present reaction is underway in this laboratory.

Acknowledgments

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6. *Typical procedure for desulfonyloxyiodonation of arenesulfonic acid*: Method A: To a solution of *p*-toluenesulfonic acid (1.0 mmol), *o*-iodobenzoic acid (0.1 mmol), and *m*CPBA (65% purity, 1.1 mmol) in CH_3CN (3 mL) was added I_2 (1.2 mmol). The mixture was stirred for 8 h under dark conditions at 50 °C. Then the reaction mixture was poured into saturated aq Na_2SO_3 solution and extracted with ethyl acetate (15 mL × 3). The organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel (eluent: hexane) to afford pure 4-iodotoluene in 61% yield.
Typical procedure for desulfonyloxyiodonation of arenesulfonic acid: Method B: A solution of benzenesulfonic acid (1.0 mmol), *o*-iodobenzoic acid (1.1 mmol), and *m*CPBA (65% purity, 1.1 mmol) in CH_3CN (3 mL) was stirred for 1.5 h at room temperature. Then, I_2 (1.2 mmol) was added. The obtained mixture was stirred for 8 h under dark conditions at refluxing conditions. Then the reaction mixture was poured into saturated aq Na_2SO_3 solution and extracted with ethyl acetate (15 mL × 3). The organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel (eluent: hexane) to afford pure iodobenzene in 40% yield.
4-Iodotoluene: mp 34–35 °C (commercial, mp 33–35 °C). IR (nujol): 2928, 1479, 1012, 796 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.29 (3H, s), 6.92 (2H, d, J = 8.2 Hz), 7.56 (2H, d, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.99, 90.17, 131.17, 137.19, 137.42.
Iodobenzene: oil. IR (neat): 729, 684 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.11 (t, J = 7.7 Hz, 2H), 7.32 (t, J = 7.7 Hz, 1H), 7.70 (d, J = 7.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 94.38, 127.45, 130.24, 137.47.
1,3-Diiodo-2,4,6-trimethylbenzene: mp 79–80 °C (lit.[8] 82 °C). IR (KBr): 2975, 1440, 1375, 860 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.42 (6H, s), 2.92 (3H, s), 7.00 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 29.88, 39.54, 101.16, 127.89, 141.83, 144.11; MS (APPI): m/z [M^+] calcd for $C_9H_{10}I_2$: 371.8866; found: 371.8869.
1,3,5-Triiodo-2,4,6-trimethylbenzene: mp 205–206 °C (lit.[8] 206–207 °C). IR (nujol): 1328, 1514, 936, 605 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.01 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 39.54, 101.16, 144.11; MS (APPI): m/z [M^+] calcd for $C_9H_9I_3$: 497.7833; found: 497.7837.
1,4-Diiodo-2,5-dimethylbenzene: mp 102–103 °C (lit.[9] mp 103–104 °C). IR (KBr): 2980, 1470, 1330, 880 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.34 (6H, s), 7.65 (2H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.85, 100.60, 139.22, 140.61; MS (APPI): m/z [M^+] calcd for $C_8H_8I_2$:357.8710; found: 357.8712.
1-Iodo-2,5-dimethylbenzene: oil (lit.[8] oil). IR (neat): 2918, 1487, 1034, 808 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.23 (3H, s), 2.38 (3H, s), 7.04 (1H, d, J = 8.0 Hz), 7.11 (1H, d, J = 8.0 Hz), 7.65 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.27, 27.48, 101.03, 128.94, 129.34, 137.17, 138.12, 139.29; MS (APPI): m/z [M^+] calcd for C_8H_9I: 231.9743; found: 231.9746.
1,5-Diiodo-2,4-dimethylbenzene: mp 70–71 °C (lit.[10] mp 71–72 °C). IR (KBr) 2980, 1470, 1330, 880 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.37 (6H, s), 7.09 (1H, s), 8.17 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 27.36, 97.79, 130.73, 141.42, 147.09; MS (APPI): m/z [M^+] calcd for $C_8H_8I_2$: 357.8710; found: 357.8713.
2,4-Dimethyl-1-iodobenzene: oil (lit.[8] oil). IR (neat): 2917, 1490, 1034, 809 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.26 (3H, s), 2.38 (3H, s), 6.69 (1H, d, J = 8.0 Hz), 7.06 (1H, s), 7.66 (1H, d, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.83, 27.90, 96.98, 128.32, 130.75, 138.06, 138.61, 140.99; MS (APPI): m/z [M^+] calcd for C_8H_9I: 234.9743; found: 231.9747.
4-Iodo-1-chlorobenzene: mp 54–55 °C (commercial, mp 53–54 °C). IR (nujol): 2923, 1469, 1377, 1091, 1006, 809 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.08 (2H, d, J = 8.6 Hz), 7.61 (2H, d, J = 8.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 91.13, 130.53, 134.19, 138.77.
1,2-Diiodo-4-methylbenzene: oil. IR (neat): 2916, 1449, 1001, 807 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 2.24 (3H, s), 6.84 (1H, dd, J = 1.4, 8.2 Hz), 7.71 (1H, d, J = 8.2 Hz), 7.72 (1H, d, J = 1.4 Hz,); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.46, 103.55, 107.69, 130.34, 138.93, 139.52, 140.05; MS (APPI): m/z [M^+] calcd for $C_7H_6I_2$: 343.8553; found: 343.8554.
4-Ethyl-1-iodobenzene: oil. IR (neat): 2964, 1484, 1006, 818 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 1.21 (3H, t, J = 7.7 Hz), 2.59 (2H, q, J = 7.7 Hz), 6.95 (2H, d, J = 8.2 Hz), 7.59 (2H, d, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.43, 28.39, 90.51, 130.01, 137.28, 143.80; MS (APPI): m/z [M^+] calcd for $C_8H_9I_1$: 231.9743; found: 231.9743.
4-(2′-Bromoethyl)-1-iodobenzene: oil. IR (neat): 2961, 1484, 1007, 803 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.10 (2H, t, J = 7.7 Hz), 3.53 (2H, t, J = 7.7 Hz), 6.97 (2H, d, J = 8.2 Hz), 7.64 (2H, d, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 32.46, 38.67, 92.26, 130.68, 137.64, 138.38; MS (APPI): m/z [M^+] calcd for C_8H_8BrI: 309.8849; found: 309.8848.
1-Iodonaphthalene: oil (commercial, mp 9 °C). IR (neat): 3051, 1556, 1498 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.17 (1H, t, J = 7.7 Hz), 7.51 (1H, t, J = 8.2 Hz), 7.57 (1H, t, J = 8.2 Hz), 7.76 (1H, d, J = 7.7 Hz), 7.82 (1H, d, J = 8.2 Hz), 8.02–8.12 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 99.57, 126.66, 126.79, 127.65, 128.49, 128.93, 132.06, 134.05, 134.28, 137.36.
1-Iodo-4-octylbenzene: oil. IR (neat): 2925, 1483, 1006, 795 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.56 (2H, d, J = 1.21 (3H, t, J = 7.70 Hz), 1.18–1.36 (m, 10H), 1.51–1.61 (m, 2H), 8.2 Hz), 2.52 (2H, t, J = 7.7 Hz), 6.99 (2H, d, J = 8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.11, 22.65, 29.18, 29.22, 29.41, 31.28, 31.85, 35.42, 90.49, 130.52, 137.18, 142.46; MS (APPI): m/z [M^+] calcd for $C_{14}H_{21}I$: 316.0682; found: 316.0682.
1-Iodo-4-dodecylbenzene (mixture): oil. IR (neat): 2925, 1483, 1464, 1006, 818 cm^{-1}; MS (APPI): m/z [M^+] calcd for $C_{18}H_{29}I$: 372.1308; found: 372.1314.
1,5-Diiodo-2-methoxybenzene: mp 67.5–68.5 °C (lit.[11] mp 68–69 °C); IR (KBr) 2930, 1565, 1470, 1280, 800 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) d = 3.85 (3H, s), 6.58 (1H, d, J = 8.7 Hz), 7.57 (1H, dd, J = 8.7, 2.0 Hz), 8.04 (1H, d, J = 2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 56.41, 83.23, 87.36, 112.75, 138.17, 146.60, 158.14; MS (APPI): m/z [M^+] calcd for $C_7H_6OI_2$: 359.8503; found: 359.8495.
7. A referee pointed out that the present reaction proceeds through the desulfonation of arenesulfonic acids to form arenes, followed by iodination of the arenes formed. However, when *p*-iodotoluene was treated with I_2 (1.2 equiv)/*m*CPBA (1.1 equiv)/*o*-iodobenzoic acid (0.1 equiv) in acetonitrile at 50 °C for 8 h under the same conditions, *p*-iodotoluene was recovered in high yield and 1,2-diiodo-4-methylbenzene was not formed at all. Based on these results and entries 25 and 26, we believe the present reaction proceeds through the reaction mechanism shown in Scheme 1.
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