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Synthesis of Aryl Iodides from Arylhydrazines and Iodine

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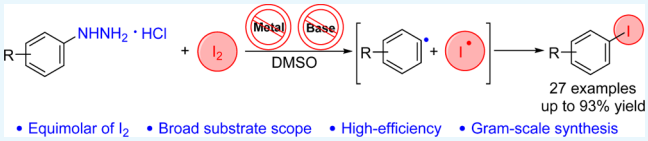
Supporting Information

ABSTRACT: A metal- and base-free method is developed for the synthesis of aryl iodides from arylhydrazine hydrochlorides and iodine. A wide variety of aryl iodides can be conveniently synthesized by an equimolar reaction of arylhydrazine hydrochlorides and I_2 in dimethyl sulfoxide at 60 °C for 6 h. In the iodination step, arylhydrazines are oxidized by iodine to form arenediazonium salts, which undergo single-electron transfer from iodide anion to give aryl and iodine radicals; subsequent combination of them affords the corresponding aryl iodides.



INTRODUCTION

Aryl iodides are important synthetic building blocks in organic chemistry that are mainly used for cross-coupling and related reactions,[1] such as the Mizoroki−Heck reaction,[2] Sonogashira coupling,[3] Suzuki−Miyaura cross-coupling,[4] and Ullmann condensation.[5] Besides, aryl iodides are employed in metal−iodine exchange using organometallic reagents such as Grignard reagents[6] and in halogen exchange via the halogenation of diaryliodonium salts with cuprous halides.[7] In addition, hypervalent iodine compounds, which are important oxidizing agents, are usually synthesized from aryl iodides.[8] Furthermore, arenes bearing radioactive iodine isotopes (^{123}I, ^{124}I, ^{125}I, and ^{131}I) play an important role in labeling biomacromolecules, such as proteins, nucleic acids, and cell surfaces in nuclear medicine and radiotherapy science.[9]

Over the past several decades, many methodologies for aromatic iodination have been developed: (1) direct aromatic iodination with I_2 or other iodination reagents such as *N*-iodosuccinimide;[10] (2) aromatic iodination by using activated precursors such as aryl boronic acid,[11] aryl triflates,[12] phenylazocarboxylates,[13] aryl carboxylic acids,[14] potassium aryltrifluoroborates,[15] and aryl diazonium salts;[16] (3) halogen exchange via an aromatic Finkelstein reaction.[17] Among these, the Sandmeyer reaction is a classical reaction that proceeds via the diazotization of aromatic amines, followed by iodination with iodides (Scheme 1, eq 1). This method does not require transition metals; however, nitrous acid, which is highly corrosive, and a strongly acidic medium, such as sulfuric acid, hydrochloric acid, or tetrafluoroboric acid are inevitable for the diazotization step.[18] Therefore, developing a facile approach to generate diazonium salts without transition metals, corrosive acids, and harsh oxidants or reductants is highly desirable.

Recently, we used commercially available arylhydrazine hydrochlorides as the source of aryl radicals and successfully achieved the arylation of aminoheterocycles and aromatic diamines, as well as the synthesis of unsymmetrical diaryl sulfides and selenides (Scheme 1, eq 2).[19] Inspired by the results, we explored the reaction of arylhydrazines with iodine to synthesize aryl iodides (Scheme 1, eq 3). Joshi's group reported a similar method (Scheme 1, eq 4), but it is applicable only to nitrophenylhydrazines and afforded the corresponding products in moderate yields (54−68%).[20] By contrast, our method requires mild conditions, has a much broader substrate scope, and tolerates a wide range of functional groups; further, the desired aryl iodides are formed in good to excellent yields (74−95%). Besides, compared to the Sandmeyer reaction, our protocol is safer, easier to execute, involves simpler work-up, and has higher efficiency.

RESULTS AND DISCUSSION

Initially, the cesium carbonate (Cs_2CO_3)/dimethyl sulfoxide (DMSO) system, which was used for the generation of aryl radicals in our previous work,[19] was employed for the present iodination reaction. 4-Chlorophenylhydrazine hydrochloride (**1a**, 0.5 mmol) was chosen as the model substrate for reaction with I_2 (1.0 equiv) in the presence of Cs_2CO_3 (1.0 equiv) as the base and DMSO as the solvent in the air, and 1-chloro-4-

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Scheme 1. Aromatic Iodination

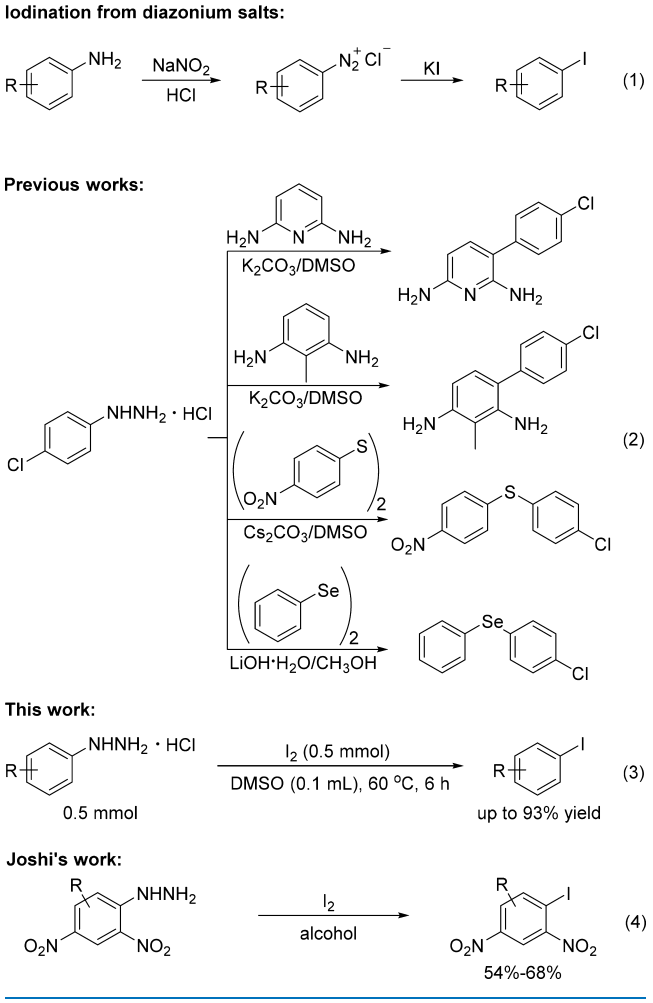
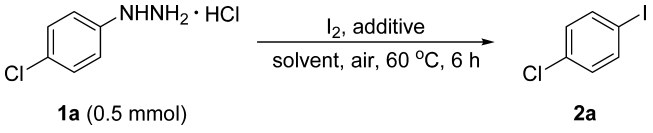


Table 1. Optimization of Reaction Conditions for Iodination of Arylhydrazines with Iodine[a]



1a (0.5 mmol) **2a**

entry	I_2 (mmol)	additive (mmol)	solvent (mL)	yield[b] (%)
1[g]	0.5	Cs_2CO_3 (0.5)	DMSO (1.5)	63, 43[c], 57[d]
2	0.5	Cs_2CO_3 (0.5)	DMF (1.5)	50
3	0.5	Cs_2CO_3 (0.5)	DMA (1.5)	38
4	0.5	Cs_2CO_3 (0.5)	CH_3CN (1.5)	35
5	0.5	Cs_2CO_3 (0.5)	acetone (1.5)	29
6	0.5	Cs_2CO_3 (0.5)	MeOH (1.5)	28
7	0.5	Cs_2CO_3 (0.5)	$CHCl_3$ (1.5)	13
8	0.5	Cs_2CO_3 (0.5)	toluene (1.5)	14
9	1.0	Cs_2CO_3 (0.5)	DMSO (1.5)	61
10	0.5	Cs_2CO_3 (0.5)	DMSO (0.5)	68
11	0.5	Cs_2CO_3 (0.5)	DMSO (0.25)	58
12	0.5	Cs_2CO_3 (0.75)	DMSO (0.5)	36
13	0.5	none	DMSO (0.5)	54
14[h]	1.0	none	DMSO (0.5)	84, 83[e], 78[f]
15	1.0	none	DMSO (0.1)	92
16	0.5	none	DMSO (0.1)	92 (87)
17	0.3	none	DMSO (0.1)	82

[a]Conditions: **1a**, I_2, additive, and solvent were stirred at 60 °C for 6 h in the air. [b]Determined by ^{1}H NMR using an internal standard 1,3,5-trioxane (isolated yield). [c]Reaction temperature was 40 °C. [d]Reaction temperature was 80 °C. [e]Reaction time was 4 h. [f]Reaction time was 8 h. [g]In this reaction, azide and aniline, besides aryl iodide, were generated as byproducts. After the reaction, arylhydrazine was already consumed but I_2 was not consumed. Most probably, air acted as an oxidant for this iodination. [h]Iodine not only acts as iodination reagent but also oxidizes phenylhydrazines to diazonium salt, and therefore excessive iodine is more beneficial to the iodination.

iodobenzene **2a** was obtained in 63% yield (Table 1, entry 1). A lower or higher reaction temperature (40 or 80 °C) gave **2a** in reduced yield (Table 1, entry 1, footnotes c and d). Screening of the solvent effects demonstrated that DMSO was the best solvent for this iodination (Table 1, entries 2−8). Increasing the amount of I_2 (2.0 equiv) failed to improve the yield of **2a** (Table 1, entry 9). A higher concentration of reactants led to the slightly improved yield of **2a** (Table 1, entry 10), but the exorbitant reaction concentration with the same equivalent of Cs_2CO_3 was sluggish for the generation of **2a** (Table 1, entry 11). Interestingly, a greater amount of Cs_2CO_3 hindered the formation of **2a** (Table 1, entry 12), and conversely, the reaction without the base afforded **2a** in 54% yield (Table 1, entry 13). Encouraged by this result, we hypothesized that no additional base was required for the generation of aryl radicals in this reaction, as opposed to our previous work.[19] Hence, we further optimized the iodination conditions in the absence of the base. As expected, the use of 2.0 equiv of I_2 gave **2a** in 84% yield (Table 1, entry 14). A shorter reaction time furnished **2a** in a similar yield (Table 1, entry 14, footnote e), whereas a longer reaction time lowered the yield of **2a** slightly (Table 1, entry 14, footnote f). Moreover, upon reducing the amount of DMSO to 0.1 mL, the desired product **2a** was furnished in 92% yield (Table 1, entry 15). With this substrate concentration, the use of the same equivalent of iodine gave **2a** in 92% yield (Table 1, entry 16), which was chosen as the optimized condition for this iodination reaction. Under the optimized condition, a clear dark red solution was formed and gas bubbles appeared. After the reaction was finished, the color of iodine does not disappear and the resulting mixture caused a foul odor, suggests the formation of dimethyl sulfide. Further decreasing the concentration (equivalents) of iodine gave **2a** in a slightly reduced yield (Table 1, entry 17).

With the optimized reaction conditions in hand (Table 1, entry 16), we next investigated a series of phenylhydrazine hydrochlorides to synthesize aryl iodides (Table 2). First, substrates with a chloro-substituent at the para-, ortho-, and meta-positions were examined and the corresponding aryl iodides were isolated in high yields (Table 2, **2a**−**2c**). Substrates with other halo-substituents (iodo, bromo, and fluoro) at the para-position were also tested under these reaction conditions; **2d** and **2e** were formed in high yields, but the volatile product **2f** was generated in somewhat low isolated yield. A similar scenario was encountered during the purification of iodobenzene, which decreased the yield of the isolated product **2g** (70% yield). Substrates with a methyl-substituent at the ortho-, meta-, and para-position, and an ethyl-substituent at the ortho-position gave the corresponding aryl iodides **2h**−**2k** in good to excellent yields. The reaction of 4-methoxyphenylhydrazine hydrochloride gave the product **2l** in 90% yield. Besides, a gram-scale iodination of 4-methoxyphenylhydrazine hydrochloride was performed under the standard conditions (Table 2, **2l**[b]) and 1.44 g (6.15 mmol,

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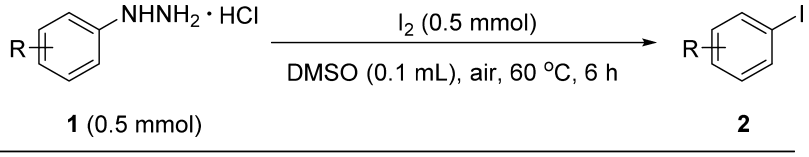
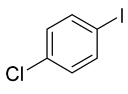
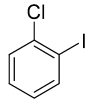
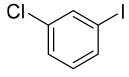
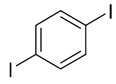
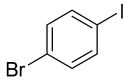
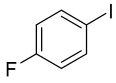
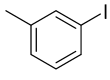
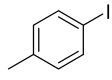
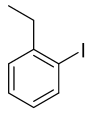
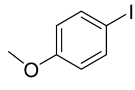
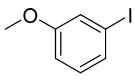
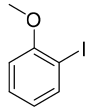
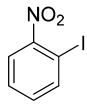
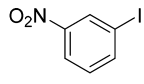
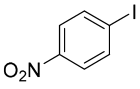
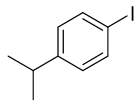
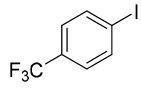
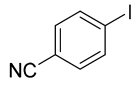
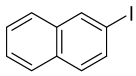
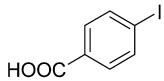
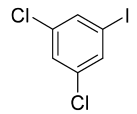
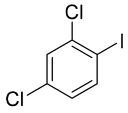
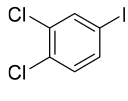
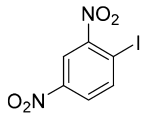
Table 2. Substrate Scope[a]



 **2a**: 87% (92%)	 **2b**: 85% (91%)	 **2c**: 85% (89%)	 **2d**: 85% (82%)[c]
 **2e**: 83% (90%)	 **2f**: 64% (89%)	 **2g**: 70% (89%)	 **2h**: 72% (75%)
 **2i**: 75% (75%)	 **2j**: 82% (88%)	 **2k**: 71% (70%)	 **2l**: 90% (95%) **2l**: 88%[b]
 **2m**: 67% (75%)[c]	 **2n**: 61% (74%)[c]	 **2o**: 87% (84%)	 **2p**: 84% (86%)
 **2q**: 74% (80%)[c]	 **2r**: 90% (95%)	 **2s**: 73% (88%)	 **2t**: 90% (85%)[c]
 **2u**: 86% (81%)	 **2v**: 72% (81%)[c]	 **2w**: (16%)	 **2x**: 87% (80%)
 **2y**: 92% (89%)	 **2z**: 93% (86%)	 **2a'**: 78% (71%)[c]	 **2b'**: 0%

[a]Yield of isolated product is based on **1** (^{1}H NMR yield using an internal standard 1,3,5-trioxane). [b]Gram scale. [c]DMSO (0.2 mL) was used.

88% isolated yield) of **2l** was formed from 7 mmol of the starting compound (1.22 g). 3-Methoxy- and 2-methoxy substituents were also tolerated under these reaction conditions (Table 2, **2m** and **2n**). Substrates with electron-withdrawing groups such as the nitro group at the ortho-, meta-, and para-positions (**1o**−**1q**), as well as 4-trifluoromethyl (**1s**), 4-cyano (**1t**), and 4-carboxyl (**1v**) moieties could be iodinated to afford the corresponding products in good to excellent yields. 4-Isopropylphenylhydrazine hydrochloride also afforded **2r** in excellent yield. Furthermore, 2-iodonaphthalene **2u** was generated in good yield under these iodination conditions but the formation of 2-iodopyridine **2w** did not proceed well probably due to the presence of the basic pyridyl group. Disubstituted substrates, i.e., substrates with 3,5-dichloro-, 2,4-dichloro-, 3,4-dichloro-, and 2,4-dinitro substituents, could be employed under the standard reaction

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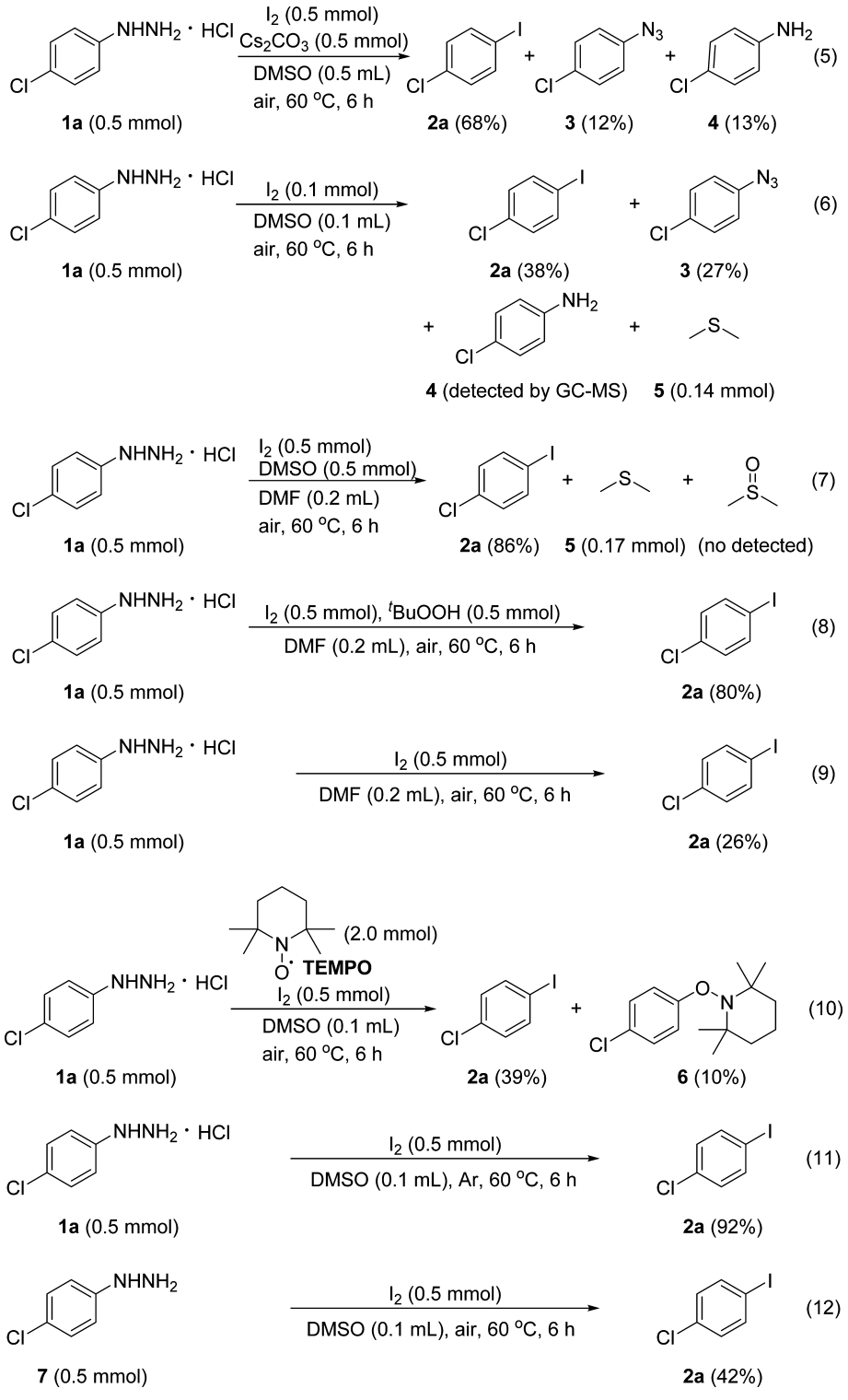
Scheme 2. Control Experiments



conditions to afford the desired products in good to excellent yields (Table 2, **2x**−**2a′**). Unfortunately, when an aliphatic hydrazine such as *tert*-butylhydrazine hydrochloride was employed as substrate, **2b′** was not formed under the standard condition.

For a better understanding of this iodination reaction, several control experiments were conducted, as shown in Scheme 2 (eqs 5−12). During the optimization of the reaction conditions, we found that 1-azido-4-chlorobenzene **3** and 4-chloroaniline **4** were generated as byproducts in the presence of a base (Scheme 2, eq 5). Under the standard reaction conditions, when the amount of I_2 was decreased to 0.1 mmol, aryl iodide **2a**, azide **3**, aniline **4**, and dimethyl sulfide **5** were detected by ^{1}H NMR analysis of the crude mixture. Besides, the formation of azide **3** and aniline **4** could be further confirmed by gas chromatography−mass spectrometry (Scheme 2, eq 6). As well known, DMSO can oxidize hydrogen iodide to iodine, whereas dimethyl sulfide is

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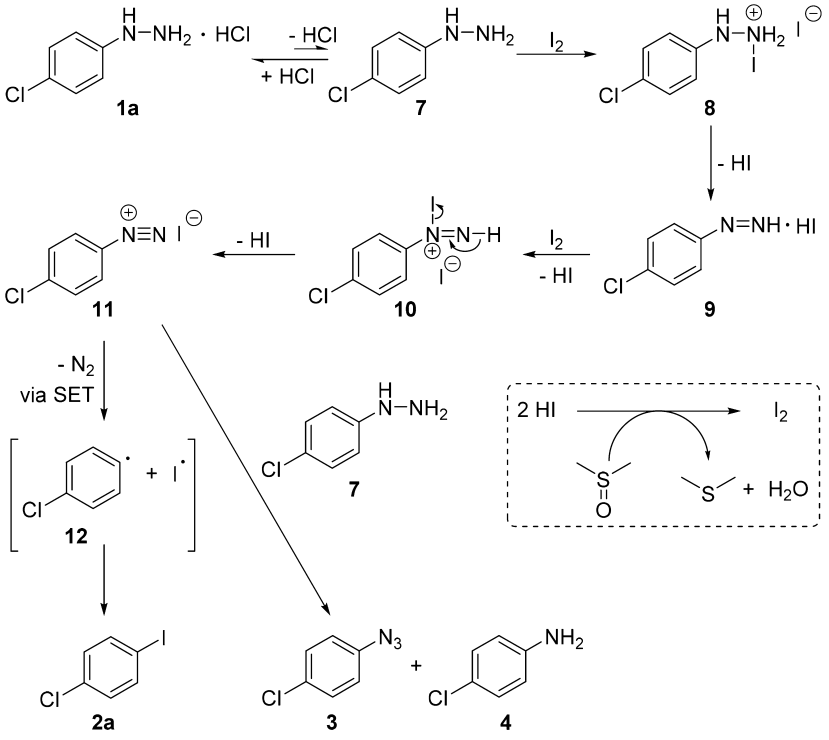
Scheme 3. Possible Pathway for the Synthesis of Aryl Iodides



generated as the reduction product.[21] Therefore, we speculated that hydrogen iodide may be generated during this iodination, which further confirms that acidic conditions favor this reaction. To clarify the role of DMSO in the iodination reaction, dimethylformamide was used as the solvent in combination with 0.5 mmol DMSO (Scheme 2, eq 7); 86% of **2a** was formed along with 0.17 mmol of dimethyl sulfide **5** (which was detected by the crude ^{1}H NMR spectra), whereas DMSO was not detected after the iodination reaction was finished. The reaction with 0.5 mmol of *tert*-butyl hydroperoxide (^{t}BuOOH) as an oxidant instead of DMSO also afforded **2a** in 80% yield (Scheme 2, eq 8). In contrast, the iodination in the absence of DMSO only yielded 26% of **2a** (Scheme 2, eq 9). These results suggest that DMSO acted as not only solvent but also co-oxidant during the iodination reaction: comparing the results of eqs 7, 9, and 11, DMSO seems to be the major oxidant in this iodination reaction. In addition, when the radical scavenger (2,2,6,6-tetramethylpiperidin-1-yl)oxyl was added to the reaction mixture under the standard conditions (Scheme 2, eq 10), **2a** was formed in a low yield with 10% of **6**, which implies that the iodination proceeds through a free-radical pathway. Besides, this reaction can proceed well under argon protection (Scheme 2, eq 11), suggesting that the oxidation of arylhydrazine to aryl radical can proceed not only with molecular oxygen but also iodine itself. Free 4-chlorophenylhydrazine **7** was also employed as a substrate for the iodination reaction but only to generate 42% of **2a**, which implied that acidic condition is essential for stabilizing arylhydrazine under this iodination reaction (Scheme 2, eq 12).

On the basis of these control experiments, a mechanism for the iodination is proposed, as shown in Scheme 3. Specifically, the starting material **1a** produces the free 4-chlorophenylhydrazine **7**, which reacts with iodine to afford intermediate **8**. Dehydroiodination of **8** leads to **9**, which further reacts with iodine to form **10**. Charge transfer of **10** affords diazonium salt **11**, which upon single-electron transfer (SET) and nitrogen release, generates phenyl radical **12** and an iodine radical. The combination of the phenyl and iodine radicals leads to the formation of aryl iodide **2a**. Excess amount of **7** (free form) may react with diazonium salt **11** to generate byproducts **3** and **4**.[22] During this iodination, hydrogen iodide can be oxidized to iodine by DMSO with the release of dimethyl sulfide.[21]

CONCLUSIONS

In summary, we have developed a facile and efficient method to synthesize aryl iodides from arylhydrazine hydrochlorides and iodine in the absence of any metal catalysts and additives. During this iodination, iodine plays a dual role: (1) an oxidant for converting arylhydrazines to arenediazonium salts, which subsequently undergo SET to form aryl radicals; (2) an iodination reagent to afford aryl iodides. Arylhydrazine hydrochlorides with a diverse range of functional groups are tolerated under these iodination conditions, and the corresponding aryl iodides are obtained in good to excellent yields. Further studies on halogenation of the arylhydrazine hydrochlorides using other halogenation reagents are underway, and the results will be reported in due course.

EXPERIMENTAL SECTION

General Remarks. Unless otherwise stated, all starting materials and solvents were purchased from commercial sources and used without further purification. ^{1}H NMR spectra were recorded on JEOL JNM-ECS400 (400 MHz) FT NMR system or JEOL JNM-ECX400 (400 MHz) FT NMR system in $CDCl_3$ and DMSO-d_6 with Me_4Si as an internal standard. ^{13}C NMR spectra were recorded on JEOL JNM-ECX400 (100 MHz) FT NMR or JEOL JNM-ECS400 (100 MHz) FT NMR in $CDCl_3$ and DMSO-d_6.

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General Procedure for the Synthesis of Aryl Iodides (2). The desired arylhydrazine hydrochloride derivatives **1** (0.5 mmol), I_2 (126.9 mg, 0.5 mmol), and DMSO (0.1 mL) were added to a round-bottomed flask, and the reaction mixture was stirred at 60 °C for 6 h under air. The resulting mixture was cooled to room temperature and then sat. $Na_2S_2O_8$ (aq, 5 mL) and water (10 mL) were added. The mixture was extracted with $CHCl_3$ (4 × 5 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. Finally, the residue was purified by silica gel chromatography (eluent: hexane/ethyl acetate) to give **2** (eluent for **2v**: chloroform/methanol).

*1-Chloro-4-iodobenzene (**2a**).* [CAS: 637-87-6].[23] White solid, 103.7 mg, 87% (isolated yield), mp 52−53 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 8.8 Hz, 2H), 7.08 (d, J = 8.8 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 138.9, 134.6, 130.7, 91.3; MS (EI) $[M]^+$ m/z = 238.

*1-Chloro-2-iodobenzene (**2b**).* [CAS: 615-41-8].[23] Light yellow oil, 101.6 mg, 85% (isolated yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, J = 8.0 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 7.29 (t, J = 8.4 Hz, 1H), 6.96 (t, J = 8.0 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 140.4, 138.6, 129.5, 128.0, 98.2; MS (EI) $[M]^+$ m/z = 238.

*1-Chloro-3-iodobenzene (**2c**).* [CAS: 625-99-0].[23] Light yellow oil, 102.0 mg, 85% (isolated yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (t, J = 1.8 Hz, 1H), 7.59 (dq, J = 7.6, 0.9 Hz, 1H), 7.32 (dq, J = 8.4, 1.1 Hz, 1H), 7.03 (t, J = 8.2 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 137.3, 135.8, 135.2, 131.1, 128.1, 94.1; MS (EI) $[M]^+$ m/z = 238.

*1,4-Diiodobenzene (**2d**).* [CAS: 624-38-4].[12] White solid, 145.3 mg, 85% (isolated yield), mp 126−127 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (s, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 139.5, 93.5; MS (EI) $[M]^+$ m/z = 330.

*1-Bromo-4-iodobenzene (**2e**).* [CAS: 589-87-7].[24] White solid, 117.2 mg, 83% (isolated yield), mp 87−88 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (dt, J = 8.8, 2.4 Hz, 2H), 7.23 (dt, J = 8.8, 2.4 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 139.2, 133.6, 122.3, 92.2; MS (EI) $[M]^+$ m/z = 282.

*1-Fluoro-4-iodobenzene (**2f**).* [CAS: 352-34-1].[11] Colorless oil, 71.2 mg, 64% (isolated yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60−7.65 (m, 2H), 6.84 (tt, J = 8.8, 2.6 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.8 (d, J = 249.1 Hz), 139.1 (d, J = 7.6 Hz), 117.9 (d, J = 23.0 Hz), 87.1 (d, J = 2.9 Hz); MS (EI) $[M]^+$ m/z = 222.

*Iodobenzene (**2g**).* [CAS: 591-50-4].[12] Colorless oil, 71.5 mg, 70% (isolated yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 7.6 Hz, 2H), 7.33 (t, J = 7.4 Hz, 1H), 7.11 (t, J = 7.8 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 137.6, 130.4, 127.6, 94.5; MS (EI) $[M]^+$ m/z = 204.

*1-Iodo-2-methylbenzene (**2h**).* [CAS: 615-37-2].[23] Colorless oil, 78.6 mg, 72% (isolated yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J = 7.6 Hz, 1H), 7.25−7.22 (m, 2H), 6.84−6.88 (m, 1H), 2.43 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 141.5, 139.1, 129.9, 128.3, 127.5, 101.6, 28.3; MS (EI) $[M]^+$ m/z = 218.

*1-Iodo-3-methylbenzene (**2i**).* [CAS: 625-95-6].[23] Colorless oil, 80.9 mg, 75% (isolated yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (s, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.12 (d, J = 7.6 Hz, 1H), 6.98 (t, J = 8.0 Hz, 1H), 2.29 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 140.4, 138.2, 134.6, 130.1, 128.5, 94.5, 21.1; MS (EI) $[M]^+$ m/z = 218.

*1-Iodo-4-methylbenzene (**2j**).* [CAS: 624-31-7].[12] White solid, 90.1 mg, 82% (isolated yield), mp 31−32 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 2.29 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 137.6, 137.4, 131.3, 90.3, 21.2; MS (EI) $[M]^+$ m/z = 218.

*1-Ethyl-2-iodobenzene (**2k**).* [CAS: 18282-40-1].[25] Colorless oil, 82.1 mg, 71% (isolated yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (dd, J = 8.3, 1.6 Hz, 1H), 7.21−7.30 (m, 2H), 6.87 (td, J = 8.3, 1.6 Hz, 1H), 2.73 (q, J = 7.5 Hz, 2H), 1.21 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 146.6, 139.5, 128.7, 128.5, 100.6, 34.3, 14.7; MS (EI) $[M]^+$ m/z = 232.

*1-Iodo-4-methoxybenzene (**2l**).* [CAS: 696-62-8].[12] White solid, 106.5 mg, 90% (isolated yield), mp 48−49 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 9.2 Hz, 2H), 6.68 (d, J = 9.2 Hz, 2H), 3.77 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 159.6, 138.3, 116.5, 82.8, 55.4; MS (EI) $[M]^+$ m/z = 234.

*1-Iodo-3-methoxybenzene (**2m**).* [CAS: 766-85-8].[23] Light yellow oil, 78.3 mg, 67% (isolated yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25−7.29 (m, 2H), 7.00 (t, J = 8.1 Hz, 1H), 6.87 (dd, J = 8.3, 1.6 Hz, 1H), 3.78 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 160.3, 130.9, 129.9, 123.1, 113.9, 94.5, 55.5; MS (EI) $[M]^+$ m/z = 234.

*1-Iodo-2-methoxybenzene (**2n**).* [CAS: 529-28-2].[23] Light yellow oil, 71.5 mg, 61% (isolated yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 7.7 Hz, 1H), 7.29−7.33 (m, 1H), 6.83 (d, J = 8.2 Hz, 1H), 6.71 (t, J = 7.6 Hz, 1H), 3.88 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.2, 139.6, 129.7, 122.6, 111.1, 86.1, 56.4; MS (EI) $[M]^+$ m/z = 234.

*1-Iodo-2-nitrobenzene (**2o**).* [CAS: 609-73-4].[26] Yellow solid, 108.6 mg, 87% (isolated yield), mp 48−49 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 8.3 Hz, 1H), 7.87 (d, J = 8.3 Hz, 1H), 7.50 (t, J = 7.7 Hz, 1H), 7.25−7.29 (m, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 153.1, 142.0, 133.5, 129.2, 125.6, 86.3; MS (EI) $[M]^+$ m/z = 249.

*1-Iodo-3-nitrobenzene (**2p**).* [CAS: 645-00-1].[27] Colorless oil, 106.5 mg, 84% (isolated yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (t, J = 2.0 Hz, 1H), 8.21 (dq, J = 8.8, 1.1 Hz, 1H), 8.03 (dt, J = 7.6, 1.1 Hz, 1H), 7.30 (t, J = 8.2 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 148.7, 143.6, 132.6, 130.8, 122.9, 93.6; MS (EI) $[M]^+$ m/z = 249.

*1-Iodo-4-nitrobenzene (**2q**).* [CAS: 636-98-6].[28] Yellow solid, 92.4 mg, 74% (isolated yield), mp 171−172 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 9.6 Hz, 2H), 7.91 (d, J = 9.6 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 147.9, 138.8, 125.0, 102.8; MS (EI) $[M]^+$ m/z = 249.

*1-Iodo-4-isopropylbenzene (**2r**).* [CAS: 17356-09-1].[12] Light yellow oil, 111.0 mg, 90% (isolated yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 7.9 Hz, 2H), 6.98 (d, J = 8.7 Hz, 2H), 2.80−2.90 (m, 1H), 1.23 (s, 3H), 1.21 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 148.6, 137.4, 128.8, 90.8, 33.9, 24.0; MS (EI) $[M]^+$ m/z = 246.

*1-Iodo-4-(trifluoromethyl)benzene (**2s**).* [CAS: 455-13-0].[29] Colorless oil, 99.0 mg, 73% (isolated yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 7.7 Hz, 2H), 7.35 (d, J = 8.2 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 138.2, 130.3 (q, J = 33.0 Hz), 127.0 (q, J = 3.8 Hz), 124.1 (q, J = 272.2 Hz), 98.7; MS (EI) $[M]^+$ m/z = 272.

*4-Iodobenzonitrile (**2t**).* [CAS: 3058-39-7].[28] White solid, 103.4 mg, 90% (isolated yield), mp 124−125 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 7.9 Hz, 2H), 7.37 (d, J = 7.9 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 138.6, 133.3, 118.3, 111.9, 100.4; MS (EI) $[M]^+$ m/z = 229.

*2-Iodonaphthalene (**2u**).* [CAS: 612-55-5].[28] Light yellow solid, 110.7 mg, 86% (isolated yield), mp 49−50 °C; ^{1}H NMR

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(400 MHz, $CDCl_3$): δ 8.24 (s, 1H), 7.80 (q, J = 3.2 Hz, 1H), 7.72 (dt, J = 9.6, 1.6 Hz, 2H), 7.58 (d, J = 8.8 Hz, 1H), 7.51−7.47 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 136.7, 135.1, 134.5, 132.2, 129.6, 128.0, 126.9, 126.8, 126.6, 91.6; MS (EI) $[M]^+$ m/z = 254.

*4-Iodobenzoic Acid (**2v**).* [CAS: 619-58-9].[23] White solid, 89.1 mg, 72% (isolated yield), mp 269−270 °C; ^1H NMR (400 MHz, DMSO-d_6): δ 13.04 (br, 1H), 7.88 (d, J = 8.3 Hz, 2H), 7.69 (d, J = 8.7 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 166.9, 137.6, 131.1, 130.3, 101.2; MS (EI) $[M]^+$ m/z = 248.

*1,3-Dichloro-5-iodobenzene (**2x**).* [CAS: 3032-81-3].[27] White solid, 119 mg, 87% (isolated yield), mp 49−50 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, J = 1.6 Hz, 2H), 7.34 (t, J = 2.0 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 135.7, 128.5, 93.8; MS (EI) $[M]^+$ m/z = 272.

*2,4-Dichloro-1-iodobenzene (**2y**).* [CAS: 29898-32-6].[30] Colorless oil, 125.1 mg, 92% (isolated yield); ^1H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.2 Hz, 1H), 7.46 (d, J = 2.3 Hz, 1H), 6.96 (dd, J = 8.7, 2.3 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 140.9, 139.6, 135.2, 129.4, 128.5, 95.6; MS (EI) $[M]^+$ m/z = 272.

*1,2-Dichloro-4-iodobenzene (**2z**).* [CAS: 20555-91-3].[27] White solid, 126.6 mg, 93% (isolated yield), mp 30−31 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 1.8 Hz, 1H), 7.51 (dd, J = 8.5, 2.1 Hz, 1H), 7.16 (d, J = 8.7 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 138.9, 136.9, 133.8, 132.8, 131.9, 91.1; MS (EI) $[M]^+$ m/z = 272.

*1-Iodo-2,4-dinitrobenzene (**2a′**).* [CAS: 709-49-9].[24] Yellow solid, 114.4 mg, 78% (isolated yield), mp 83−84 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 8.68 (d, J = 2.4 Hz, 1H), 8.31 (d, J = 8.8 Hz, 1H), 8.11 (dd, J = 8.8, 2.4 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 153.3, 148.1, 143.5, 127.1, 120.5, 94.9; MS (EI) $[M]^+$ m/z = 294.

General Procedure for the Gram-Scale Synthesis of 1-Iodo-4-methoxybenzene (2l). 4-Methoxyphenylhydrazine hydrochloride **1l** (1.22 g, 7 mmol), I_2 (1.80 g, 7 mmol), and DMSO (1.4 mL) were added to a round-bottomed flask, and the reaction mixture was stirred at 60 °C for 6 h under air. The resulting mixture was cooled to room temperature, and then sat. $Na_2S_2O_8$ (aq, 25 mL) and water (100 mL) were added. The mixture was extracted with $CHCl_3$ (4 × 20 mL), dried over anhydrous Na_2SO_4, and concentrated in vacuo. Finally, the residue was purified by silica gel chromatography (eluent: hexane/ethyl acetate) to give **2l** (1.44 g).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b01559.

^1H NMR and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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