ELECTRON-RICH AROMATICS UNDER BALL MILLING: OXIDATIVE ARYL-IODINATION USING I$_2$-OXONE AND BIARYLATION WITH I$_2$

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GRAPHICAL ABSTRACT

Abstract We report here a simple, efficient, and environmentally friendly methodology for electrophilic aryl-iodination of electron-rich arenes using I$_2$-oxone under ball milling. The reactions work efficiently under solvent-free conditions at room temperature. We have also shown that iodine could be used as catalyst for metal-free biaryl coupling of a few electron-rich substrates. In addition, one-pot multistep synthesis has been demonstrated for one substrate.

Keywords Ball milling; biarylation; iodination; mechanochemistry; solvent-free synthesis

INTRODUCTION

With growing public concern over “alternative energy input”[1] it is essential to trim the usage of chemicals in routine chemical synthesis. Therefore eliminating waste and developing economical methodologies are important aspects of doing reactions in a greener fashion.[2] Metal-free reagents[3] are popular in pharmaceutical/medicinal industries to avoid metal contamination in drugs, which cause side effects.[4] The aryl iodides are well recognized in organic chemistry either

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as synthetic intermediates\(^5\) or as organocatalysts.\(^6\) These iodides are easily manageable for the functional group interconversion to other labile groups during the synthesis of pharmaceutical or natural products.\(^7\) Although aryl iodination methodologies\(^8\) have been well executed for more than a century, there is still demand for better methodologies to avoid handling hazardous chemicals during aryl-iodination. We highlight a few known examples of iodinations: NIS (N-iodosuccinimide)–trifluoroacetic acid (TFA),\(^9\) NIS-In(OTf)\(_3\),\(^10\) NIS-BF\(_3\)-H\(_2\)O,\(^11\) N,N'-diiodo-N,N'-1,2-ethanediylbis(\(p\)-toluenesulphonamide),\(^12\) KI-H\(_2\)O\(_2\),\(^13\) KI-KIO\(_3\),\(^14\) ammonium iodide–oxone,\(^15\) benzyltrimethylammonium dichloro-iodate,\(^16\) I\(_2\)-H\(_2\)O\(_2\)-CeO\(_2\) nanocrystals,\(^17\) I\(_2\)/NaBO\(_3\)·4H\(_2\)O system in ionic liquid,\(^18\) I\(_2\)-AgNO\(_3\),\(^19\) and nitrogen dioxide-I\(_2\).\(^20\)

RESULTS AND DISCUSSION

Herein, we report a synthetic methodology (Scheme 1) for metal-free oxidative iodination of electron-rich arenes\(^8,21\) under solvent-free, ball-milling condition\(^,22\) at room temperature using molecular iodine and Oxone (2KHSO\(_5\)·KHSO\(_4\)·K\(_2\)SO\(_4\))\(^23\) combination. We anticipated that ball-milling methodology\(^24\) may be used not only to do iodination under nonhazardous conditions but also lead to greener approaches in organic synthesis\(^11\). Currently, we are also focusing our research interest toward developing methodologies using the ball mill.\(^25\) This methodology is found to be free from usage of toxic/hazardous chemicals, environmentally benign, and highly economical.\(^26\)

The reactions were done under ball-milling conditions (frequency 21 Hz) in a solid state and the progress of the reactions was monitored either by thin-layer chromatography (TLC) or \(^1\)H NMR. After completion of reaction, products were isolated by dissolving the reaction mixture in ethyl acetate (environmentally friendly), subsequent paper filtration, and evaporation of the solvent. The compounds were purified by chromatographic methods wherever necessary.

Our study results of iodination to aryl iodides are depicted in Fig. 1. Iodinated products of anisole, aniline, alkyl benzene, benzaldehyde, and nitrobenzene derivatives were obtained in very good to excellent yields. We now compare our method with the literature system. As shown in Fig. 1, both \(2e\) and \(2j\) were isolated as single products using I\(_2\)-oxone under ball-milling conditions. However, in the literature report, the iodination was done using N,N'-di[3,5-bis(trifluoromethyl)phenyl] thiourea in a nonselective manner.\(^27\)

\[\text{Scheme 1. Conditions and scope for iodination using molecular iodine and oxone under ball milling.}\]
This methodology was also found to be chemoselective and no benzylic iodoniation was observed for the alkyl benzenes; for example, 2d was isolated in 80% yield as a single product. In spite of poor electrophilicity of iodonium ion generated from I₂, we have shown the aryl-iodination of various types of aromatic compounds. We were also successful in iodination of nitrobenzene derivative; 2o was isolated in 52% yield. Interestingly, iodination to 2p with I₂-oxone did not lead to any oxidation to benzoic acid, although oxone is well known to oxidize aldehydes to acids. These facts clearly establish that oxone oxidizes iodine to I⁺ for oxidative aryl iodination.

Furthermore, under ball-milling condition, 2b (monoiodinated product of 1,3,5-trimethoxy benzene) was isolated in 88% yield using I₂-Oxone combination. However, with 0.5 equivalent of iodine, dimerized product 3 was obtained in 48% yield as a single product (Table 1, entry 2).
Based on the results shown in Table 1, we have proposed a mechanism for biarylation shown in Fig. 2. Electron-rich aromatic compounds form a charge transfer complex with the iodine and followed by single-electron transfer (SET)\(^{[30]}\) led to

\[
\text{ArH} + \overset{\text{l}_2}{\longrightarrow} \text{Ar-Ar} + 2\text{H}\overset{\text{I}}{\longrightarrow}
\]

\[
\text{ArH} \overset{\text{l}_2}{\longrightarrow} [\text{ArH} + \overset{\text{l}_2}{\longrightarrow}]^{+} \overset{\text{SET}}{\longrightarrow} \text{Ar}^{+} \overset{\text{ArH}}{\longrightarrow} -\text{e}^{\text{-}}, -2\text{H}^{+} \overset{\text{Ar-Ar}}{\longrightarrow}
\]

\[
\overset{\text{l}_2}{\longrightarrow} 2\text{I}^{-}
\]

![Diagram](image)

**Figure 2.** Plausible mechanism of biarylation of the compounds 3–5 via electron-transfer pathway.

**Table 1.** Iodination of trimethoxy benzene in different conditions

| Entry | Reagent   | Condition\(^{a}\) | Conversion (%) | Yield (%) |
|-------|-----------|--------------------|----------------|-----------|
| 1     | I\(_2\)-Oxone | Ball mill, 0.25 h  | 100            | 2b, 88    |
|       |           |                    |                | 3, 0      |
| 2     | I\(_2\)   | Ball mill, 9 h     | 64             | 2b, 49    |
|       |           |                    |                | 3, 28     |
| 3     | I\(_2\)-AIBN | Ball mill, 9 h     | 56             | 2b, 49    |
|       |           |                    |                | 3, 28     |
| 4     | I\(_2\)   | DCM, 24 h          | 76             | 2b, 40    |
|       |           |                    |                | 3, 0      |
| 5     | I\(_2\)   | ACN, 24 h          | 64             | 2b, 40    |
|       |           |                    |                | 3, 0      |
| 6     | I\(_2\)-Oxone | EtOAc, 16 h        | 88             | 2b, 69    |
|       |           |                    |                | 3, 0      |

\(^{a}\)All the reactions are done at room temperature. DCM, dichloromethane; ACN, acetonitrile; EtOAc, ethyl acetate.
cation radical species. This cation radical species forms adduct with another aryl compound, which finally yielded biaryl derivative after losing a single electron and two protons (I\(^-\) acts as proton acceptor). The formation charge transfer complex could be completely ruled out in polar solvents such as ethyl acetate or acetonitrile and only monoiiodinated product was obtained (Table 1, entries 4–6). However, the mixture of 2b and 3 was obtained when the reaction was done using I\(_2\)-AIBN (azobisisobutyronitrile, radical initiator) and 1,3,5-trimethoxy benzene (Table 1, entry 2). This fact may be an indication that iodide radical generated from I\(_2\)-AIBN combination could couple to aryl radical (generated from aryl radical cation) and resulted in 2b.

We have also discussed about the economic benefit for our methods over traditional ones for the synthesis of 2e. The results are shown in Fig. 3. In addition, we have established the efficiency of this methodology by doing a one-pot multistep synthesis.\(^{[31]}\) The one-pot multistep synthesis concept is a growing

![Diagram of iodination process](image)

**Figure 3.** Comparative statement on economic benefit may be obtained from our methodology over literature methods. Using 25 mL of ZrO\(_2\) jar, 1.0 g of 2-methoxy naphthalene (1e) was successfully iodinated.

| Reference | Reagents | Cost of materials used\(^{\text{a}}\) | Total cost | Time (h) | Yield(%) |
|-----------|----------|----------------------------------|------------|---------|---------|
| [14]      | NH\(_4\)I, Oxone, MeOH | NH\(_4\)I (1 g, 1.1 mmol) $0.3; Oxone (4.27 g, 1.1 mmol) $1.65; MeOH (30 mL) $1.4; DCM (filtration, 60 mL) $0.7; column purification $11.0 | $15.05 | 24 | 96 |
| [13]      | KI, KIO\(_3\), MeOH-dil. HCl | KI (1.15 g, 1.1 mmol) $0.63; KIO\(_3\) (1.49 g,1.1 mmol); $0.6; MeOH (5 mL) $0.23; DCM (extraction 75 mL) $0.88; column purification $11.0 | $13.34 | 3.5 | 72 |
| [18]      | KI, H\(_2\)O\(_2\), AcOH | KI (1.15 g, 1.1 mmol) $0.63; ethyl acetate (extraction, 100 mL) $1; column purification $11.0 | $12.63 | 8 | 99 |
| Our method | I\(_2\), Oxone, Ball-Milling | I\(_2\) (0.8 g,0.5 mmol) $0.38; Oxone (3.88 g,1.0 mmol): $1.5; ethyl acetate (filtration: 100 mL) $1; heptane (recrystallization, 50 mL): $1.5 | $4.38 | 4 | 82 |

\(^{\text{a}}\)Includes column purification: solvent (petroleum ether 600 mL) $6.5 and silica gel (60 g) $4.5.
aspect in organic chemistry because the use of bulk solvents can be avoided for purification of the intermediate formed during the course of the reaction. As can be seen from Scheme 2, iodinated product 7 of 3-methoxy benzyl alcohol (6) was isolated in 54% yield.

Although we have presented here an efficient metal-free synthetic methodology of aryl iodination of aromatic compounds but this method has certain limitations. These are (a) aniline and phenol derivatives in the presence of iodine–Oxone led to inseparable mixture of unidentified products, (b) handling of volatile substrates like mesitylene was found be difficult and therefore biarylation of mesitylene resulted in a very poor yield (5, Fig. 2), and (c) biaryl couplings with iodine was possible only for electron-rich substances.

EXPERIMENTAL

General Procedure for Monitoring the Reactions Under Ball Milling

Milling apparatus was stopped and small portion of sample was collected from the jar to study either 1H NMR / TLC. After that, the reaction was started and this operation time was excluded for reporting the reaction timing. Compounds 2e, 2i, and 2p were purified by recrystallization from hexane and compound 7 from ethanol. All other compounds were purified by column chromatography in silica gel using hexane/ethyl acetate mixture. The TLC details (Rf retension factor) are given with their characterization data.

General Procedure for Synthesis of 2,4-Dimethoxy-5-iodo-6-methylbenzaldehyde (2p)[25a] Under Ball Milling

2,4-Dimethoxy-6-methylbenzaldehyde (50 mg, 0.277 mmol), I₂ (35 mg, 0.138 mmol), Oxone (170 mg, 0.277 mmol), and one ball (15 mm diameter) were transferred to a milling jar (25 mL, zirconium oxide). The ball-milling operation was performed and the progress of reaction was monitored by TLC. After completion of the reaction, the reaction mixture was then transferred into 30 mL of ethyl acetate (EA) and the product was isolated by paper filtration. The resulting filtrate were concentrated in vacuum and recrystallized from hot hexane to isolate 49 mg

\[ \text{Scheme 2. One-pot multistep synthesis for the iodination of 3-methoxy benzyl alcohol.} \]
(yield 57%) of 2p as colorless solid; \( R_f = 0.3 \) (hexane/ethyl acetate 19:1); mp 155–157°C; IR (neat) \( \nu \): 2353, 1661, 1573, 1462, 1392, 1317, 1277, 1208, 1161, 1073, cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 10.34 (s, 1H), 6.33 (s, 1H), 3.95 (s, 3H), 2.78 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 190.40, 165.51, 162.53, 146.57, 118.68, 92.77, 87.65, 56.71, 56.13, 26.38; HRMS observed 306.9864 (calculated for [M+H]\(^+\) 306.9831). Anal. calcd. for \( \text{C}_{10}\text{H}_{11}\text{IO}_3 \): C, 39.24; H, 3.62. Found: C, 39.03; H, 3.73.

**Procedure for Synthesis of 2-Iodo-3-methoxybenzaldehyde (7)**

**Under Ball Milling**

Commercially available (3-methoxyphenyl)methanol (50 mg, 0.36 mmol), I\(_2\) (46 mg, 0.18 mmol), Oxone (222 mg, 0.36 mmol), and one ball (10 mm diameter) were transferred to a milling jar (25 mL, zirconium oxide). The ball-milling operation was performed and the progress of reaction was monitored by TLC. After completion of the reaction, the reaction mixture was then transferred into 30 mL of ethyl acetate and followed by product was isolated by paper filtration. The resulting filtrate were concentrated in vacuum and recrystallized from hot ethanol to isolate 51 mg (yield 54%) of 7 as pale yellow solid; \( R_f = 0.7 \) (hexane/ethyl acetate 19:1); mp 108–110°C (lit.\(^{[32]}\) 114–115°C); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 10.01 (s, 1H), 7.79 (d, \( J = 8.4 \) Hz, 1H), 7.42 (d, \( J = 3.2 \) Hz, 1H), 6.93–6.90 (dd, \( J_1 = 3.2 \) Hz, \( J_2 = 3.2 \) Hz, 1H), 3.84 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 195.84, 160.42, 141.17, 135.82, 123.62, 113.71, 89.93, 55.78.

**1,4-Diiodo-2,3-dimethoxynaphthalene (2k)**

Yield 72%; \( R_f = 0.7 \) (hexane/ethyl acetate 19:1); light-red solid; mp 112–113°C; IR (neat) \( \nu \): 2961, 2833, 2360, 1626, 1599, 1489, 1465, 1438, 1251, 1198, 1163, 1113, 1003 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.83–7.81 (dd, \( J_1 = 3.2 \) Hz, \( J_2 = 3.2 \) Hz, 2H), 7.48–7.46 (dd, \( J_1 = 3.2 \) Hz, \( J_2 = 3.2 \) Hz, 2H), 4.13 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 149.58, 129.31, 126.42, 124.32, 106.33, 55.96. Anal. calcd. for \( \text{C}_{12}\text{H}_{10}\text{I}_2\text{O}_2 \): C, 32.76; H, 2.29. Found: C, 32.61; H, 2.52.

**1,2-Diiodo-4,5-dimethoxybenzene (2l)**

Yield 61%; \( R_f = 0.5 \) (hexane/ethyl acetate 19:1); colorless solid; mp 115–116°C; IR (neat) \( \nu \): 2951, 2832, 1575, 1493, 1455, 1337, 1245, 1206, 1179 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.23 (s, 2H), 3.83 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 149.58, 129.31, 126.42, 124.32, 106.33, 55.96. Anal. calcd. for \( \text{C}_{8}\text{H}_{8}\text{I}_2\text{O}_2 \): C, 24.64; H, 2.07. Found: C, 24.81; H, 2.01.

**2-Iodo-4-methoxy-1,3,5-trimethylbenzene (2n)**

Yield 73%; \( R_f = 0.8 \) (hexane); colorless liquid; IR (neat) \( \nu \): 2940, 2356, 2338, 1462, 1404, 1305, 1234, 1156, 1009 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 6.96 (s, 1H), 3.67 (s, 3H), 2.43 (s, 3H), 2.39 (s, 3H), 2.22 (s, 3H); \(^{13}\)C NMR (100 MHz,
CDCl$_3$): $\delta$ 154.33, 137.47, 134.88, 130.41, 129.49, 105.73, 60.23, 29.22, 22.79, 15.90. Anal. calcd. for C$_{10}$H$_{13}$IO: C, 43.50; H, 4.75. Found: C, 43.69; H, 4.60.

1-Iodo-2,4-dimethoxy-5-nitrobenzene (2o)

Yield 52%; R$_f$ = 0.4 (hexane/ethyl acetate 4:1); off-white solid; mp 148–149°C; IR (neat) $\tilde{\nu}$ 2356, 1593, 1562, 1494, 1458, 1427, 1385, 1338, 1311, 1264, 1213, 1103, 1049 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.42 (s, 1H), 6.44 (s, 1H), 3.98 (s, 3H), 3.97 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 163.11, 156.25, 136.25, 136.94, 133.49, 95.98, 73.39, 57.13, 56.87; HRMS observed 331.9335 (calculated for [M + Na]$^+$ 331.9396). Anal. calcd. for C$_8$H$_8$NIO$_4$: C, 31.09; H, 2.61; N 4.53. Found: C, 31.33; H, 2.40; N, 4.71.

CONCLUSION

In summary, we have proposed that a wide range of electron-rich aromatic substrates are compatible for aryl iodination with this operationally simple I$_2$-Oxone combination, which works at room temperature under solvent-free conditions and does not require any aqueous workup. This methodology is environmentally benign, requires milder reaction condition, and is mostly economical. We have also explored a one-pot multistep synthesis in a certain substrate. Besides, we have shown that iodine could be used as an efficient catalyst for biaryl coupling reaction via electron-transfer mechanism. Therefore, we anticipate that our study may draw significant attention to other chemists working not only on the development of halogenation methodologies but also to researchers looking for better methods under the area of organic mechanochemistry.$^{[33]}$

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SUPPLEMENTARY MATERIAL

The supporting information file contains $^1$H NMR spectra for all the compounds and $^{13}$C NMR spectra of all the new compounds. In addition, NMR data, melting points, and references for all the literature known compounds are given. Supplemental data for this article can be accessed on the publisher’s website.

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