CO$_2$-activated NaClO-5H$_2$O enabled smooth oxygen transfer to iodoarene: a highly practical synthesis of iodosylarene

Kazunori Miyamoto,1,* Yuichiro Watanabe,1 Taisei Takagi,1 Tomohide Okada,2 Takashi Toyama,2 Shinji Imamura,3 and Masanobu Uchiyama1,4,5*

1Graduate School of Pharmaceutical Sciences, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, 113-0033, Japan
2Market Development Department, Nippon Light Metal Company, Ltd., 1-1-13 Shimbashi, Minato-ku, Tokyo, 105-8681, Japan
3R&D Department of Chemicals, Nippon Light Metal Company, Ltd., 480 Kambara, Shimizu-ku, Shizuoka 421-3203, Japan
4Cluster for Pioneering Research (CPR), RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan
5Research Initiative for Supra-Materials (RISM), Shinshu University, 3-15-1 Tokida, Ueda, Nagano 386-8567, Japan

Email: kmiya@mol.f.u-tokyo.ac.jp, uchiyama@mol.f.u-tokyo.ac.jp

We wish to dedicate this paper to the memory of Professor Kilian Muñiz, who devoted his life to the development of hypervalent iodine chemistry

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Abstract

A safe, rapid, and environmentally friendly synthesis of iodosylarene (ArIOM) has been developed using NaClO under a carbon dioxide (CO$_2$) atmosphere. Exposure of iodoarene to NaClO-5H$_2$O in acetonitrile under CO$_2$ (1 atm) resulted in the clean formation of ArIOM within 10 minutes in high yield. The absence of a base in this method enables the direct use of in-situ-generated iodosylarene not only for a variety of oxidative transformations (synthesis of sulfilimine, pentavalent bismuth, benzene adduct, etc.), but also for the synthesis of iodonium ylide and imino-$\lambda^3$-iodane in one pot.

Keywords: Iodosylbenzene; sodium hypochlorite; carbon dioxide; imino-$\lambda^3$-iodane; iodonium ylide; oxidation; benzene

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Introduction

Hypervalent iodine(III) reagents (aryl-$\lambda^3$-iodane with two heteroatom ligands) have enjoyed widespread use in modern organic synthesis as a potent, safe, and environment-friendly oxidant.\textsuperscript{1–4} Among them, iodosylbenzene (1a), which has been known since 1892, offers many advantages. These include 1) high electrophilicity & oxidizing ability toward olefins, phenols, and heteroatom (N, P, As, Sb, Bi, Se, Te, etc.) nucleophiles in the presence/absence of Lewis/Brønsted acids, 2) selective and clean oxygen donor ability to metalloporphyrins (Mn, Fe, V, etc.), yielding high-valent oxometal species L\textsubscript{n}M=O, which are present in the active center of many oxidases, and 3) versatility as a precursor not only for aryl-$\lambda^3$-iodanes with heteroatom ligands (F, OH, OR, OAc, OCOCF\textsubscript{3}, OTs, NSO\textsubscript{2}R, etc.), but also for aryl-$\lambda^3$-iodanes with carbon ligands (aryl, vinyl, alkynyl, methylide, etc.).\textsuperscript{5–8} The usual approach for the synthesis of 1a relies on the hydrolysis of (diacetoxyiodo)benzene (2a) or (dichloroiodo)benzene (3a) with aqueous NaOH (Figure 1).\textsuperscript{9–11} However, an excess amount of NaOH is required to complete the ligand exchange, and as a result, tedious work-up, including careful rinsing with large amounts of water (in order to remove remaining base), is inevitable.\textsuperscript{12} This is problematic, because 1a is light-sensitive and gradually decomposes at room temperature.\textsuperscript{5,6} In contrast, direct oxidation of iodobenzene 4a with dimethyldioxirane 5 is a fascinating alternative approach, as the only waste product is acetone, but it suffers from a low yield of 1a owing to the occurrence of over-oxidation, affording pentavalent iodylbenzene (6a).\textsuperscript{13} Herein, we report a direct base-free approach for the synthesis of 1 from iodoarene 4, making it possible to use 1a for subsequent transformations in one pot. The key to this approach is the in situ activation of NaClO-5H\textsubscript{2}O with carbon dioxide (CO\textsubscript{2}).

![Figure 1. Approaches for the synthesis of 1. (A) Typical alkaline hydrolysis approach. (B) Direct oxidation approach. (C) Present approach.](image-url)

Results and Discussion

We recently reported that NaClO-5H\textsubscript{2}O serves as an excellent oxidant for the synthesis of (diacetoxyiodo)arene 2 in the presence of acetic acid at room temperature.\textsuperscript{14} We also reported that the oxidation of 2-iodobenzoic acid 7 with NaClO-5H\textsubscript{2}O, leading to the formation of 2-iodoxybenzoic acid (IBX) 8, is
accelerated by gaseous CO₂.\textsuperscript{15,16} Encouraged by these findings, we commenced our study by examining the direct oxidation of iodobenzene (4a) with NaClO-5H₂O under a CO₂ atmosphere. Exposure of 4a to equimolar NaClO-5H₂O in MeCN at room temperature under CO₂ (1 atm) resulted in the rapid appearance (within a few minutes) of a canary yellow-colored solution, which subsequently faded. After 10 minutes, 1a was obtained in 75–78% yield as a pale-yellow solid by means of a simple suction filtration-vacuum drying sequence (Table 1, entry 1). The FT-IR analysis of 1a thus obtained showed two strong bands due to the I–O stretching vibration (ν = 525, 446 cm\textsuperscript{-1}).\textsuperscript{17} The purity was confirmed to be ≥98% by iodometric titration. Under these conditions, over-oxidized iodylbenzene (6a) was not formed. In the absence of CO₂ (under air), 1a was not formed at all (entry 2). The reaction could be readily and safely scaled up to 74 mmol (4a: 15 g) without decrease in the efficiency (entry 4). The use of MeCN was essential for this transformation: the use of either solvent-free conditions or water-immiscible solvents such as toluene, CH₂Cl₂, and AcOEt was much less effective (entries 5–8). Other polar water-miscible solvents (acetone, DMF, and THF) did not give satisfactory results (entries 9–11).\textsuperscript{18} Surprisingly, conventional 13% and 4% aqueous NaClO solution also served as an effective oxidant, but an excess amount of the reagent led to selective formation of the over-oxidized product PhIO₂ 6a, instead of 1a (entries 12–14).\textsuperscript{14,15} In contrast, Ca(ClO)₂-3H₂O did not work at all in this system, partly because of its poor solubility in MeCN (entry 15). The substitution of CO₂ with solid NaHCO₃ is potentially attractive in terms of convenience and cost, though the yield of 1a is only moderate (entry 16).

Table 1. Oxidation of iodobenzene 4a with NaClO under CO₂

<table>
<thead>
<tr>
<th>entry</th>
<th>ClO\textsuperscript{-} source (equiv)</th>
<th>solvent</th>
<th>time</th>
<th>yield (%)\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaClO-5H₂O (1.0)</td>
<td>MeCN</td>
<td>10 min</td>
<td>75–78 (3 runs)</td>
</tr>
<tr>
<td>2\textsuperscript{b}</td>
<td>NaClO-5H₂O (1.0)</td>
<td>MeCN</td>
<td>2 h</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>NaClO-5H₂O (1.0)</td>
<td>MeCN</td>
<td>10 min</td>
<td>78 (20 mmol)</td>
</tr>
<tr>
<td>4</td>
<td>NaClO-5H₂O (1.1)</td>
<td>MeCN</td>
<td>10 min</td>
<td>74 (74 mmol)</td>
</tr>
<tr>
<td>5</td>
<td>NaClO-5H₂O (1.0)</td>
<td>–</td>
<td>3 h</td>
<td>13</td>
</tr>
<tr>
<td>6</td>
<td>NaClO-5H₂O (1.0)</td>
<td>PhMe</td>
<td>12 h</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>NaClO-5H₂O (1.0)</td>
<td>CH₂Cl₂</td>
<td>12 h</td>
<td>13</td>
</tr>
<tr>
<td>8</td>
<td>NaClO-5H₂O (1.0)</td>
<td>AcOEt</td>
<td>24 h</td>
<td>32</td>
</tr>
<tr>
<td>9</td>
<td>NaClO-5H₂O (1.0)</td>
<td>acetone</td>
<td>20 min</td>
<td>0\textsuperscript{c}</td>
</tr>
<tr>
<td>10</td>
<td>NaClO-5H₂O (1.0)</td>
<td>DMF</td>
<td>20 min</td>
<td>0\textsuperscript{c}</td>
</tr>
<tr>
<td>11</td>
<td>NaClO-5H₂O (1.0)</td>
<td>THF</td>
<td>20 min</td>
<td>0\textsuperscript{c}</td>
</tr>
<tr>
<td>12</td>
<td>4% NaClO (1.1)</td>
<td>MeCN</td>
<td>60 min</td>
<td>45</td>
</tr>
<tr>
<td>13</td>
<td>13% NaClO (1.1)</td>
<td>MeCN</td>
<td>30 min</td>
<td>72</td>
</tr>
<tr>
<td>14</td>
<td>13% NaClO (2.8)</td>
<td>MeCN</td>
<td>30 min</td>
<td>0\textsuperscript{d}</td>
</tr>
<tr>
<td>15</td>
<td>Ca(ClO)₂-3H₂O (0.5)</td>
<td>MeCN</td>
<td>30 min</td>
<td>0</td>
</tr>
<tr>
<td>16\textsuperscript{b,e}</td>
<td>NaClO-5H₂O (1.1)</td>
<td>MeCN</td>
<td>2 h</td>
<td>51</td>
</tr>
</tbody>
</table>
Table 1. Continued

Unless otherwise noted, reactions were performed on 2.5–3 mmol scale in MeCN (1.5 M) under CO₂ (1 atm). aIsolated yields. bUnder air. cDecomposition of NaClO-5H₂O occurred within 10 minutes. dPhIO₂ 6a (89%, based on oxidant used) was obtained. eNaHCO₃ (1.1 eq) was used instead of CO₂.

The optimized conditions were applicable to not only the electron-deficient iodoarenes 4b–e, but also the electron-rich iodoarenes 4f–h, affording iodosylarenes 1b–h in good to high yields (Table 2). In contrast to 4b, 2-(nitro)iodobenzene 4i selectively afforded pentavalent 2-nitro(iodyl)benzene (6b), probably due to the coordination of neighboring oxygen of the nitro group, which facilitates further oxidation. It should be emphasized that the readily hydrolyzable 4-(methoxycarbonyl)iodosylbenzene 1d was selectively obtained in good yield under conventional hydrolysis conditions (Figure 1(A)) without saponification. The attempted oxidation of highly electron-deficient pentafluoriodobenzene (4j) was unsuccessful, in marked contrast to the facile oxidation of 4j in AcOH, yielding C₆F₅I(OAc)₂. Other electron-deficient substrates, (nonafluorobutyl iodide (4k) and bromobenzene (4i)), were not oxidized under these conditions.

Table 2. Scope and limitations of direct synthesis of iodosylarene 1

<table>
<thead>
<tr>
<th>Ar</th>
<th>NaClO-5H₂O (1.2 eq)</th>
<th>MeCN, rt, 10 min under CO₂</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂</td>
<td>1b 74%</td>
<td></td>
<td>1b</td>
</tr>
<tr>
<td>CF₃</td>
<td>1c 72%</td>
<td></td>
<td>1c</td>
</tr>
<tr>
<td>CO₂Me</td>
<td>1d 75%</td>
<td></td>
<td>1d</td>
</tr>
<tr>
<td>Cl</td>
<td>1e 83%</td>
<td></td>
<td>1e</td>
</tr>
<tr>
<td>Me</td>
<td>1f 78%</td>
<td></td>
<td>1f</td>
</tr>
<tr>
<td>MeO</td>
<td>1g 80%</td>
<td></td>
<td>1g</td>
</tr>
<tr>
<td>OMe</td>
<td>1h 85% (56%)</td>
<td></td>
<td>1h</td>
</tr>
<tr>
<td>NO₂</td>
<td>1i 0%</td>
<td></td>
<td>1i</td>
</tr>
<tr>
<td>Ph-Br</td>
<td>1j 0%</td>
<td></td>
<td>1j</td>
</tr>
<tr>
<td>C₆F₅-IO</td>
<td></td>
<td></td>
<td>1k</td>
</tr>
<tr>
<td>Ph-BrO</td>
<td></td>
<td></td>
<td>1f 0%</td>
</tr>
</tbody>
</table>

All reactions were performed on 3 mmol scale in MeCN (1.5 M) under CO₂ (1 atm). a30 min. bYield of 2-nitro(iodyl)benzene (6b) based on the NaClO-5H₂O used.

Gratifyingly, the base-free preparation of 1a enabled a variety of one-pot transformations (Scheme 1), as follows. 1) Direct synthesis of ylidic λ³-iodanes. In the presence of K₂CO₃, 4-nitrobenzenesulfonyl chloride (7) and dimeredone (9) underwent ligand exchange and afforded synthetically useful imino-λ³-iodane 8 and iodonium ylide 10, respectively, in good yields. 2) Rapid deprotection of dithioacetal. Oxidative hydrolysis of dithiocacetal 11 with in-situ-formed 1a proceeded at room temperature within 30 minutes to give benzaldehyde (12) in high yield. In sharp contrast, the reaction with 1a prepared by the NaOH hydrolysis method (Figure 1(A)) was very sluggish (Scheme S2 in Supporting Information). 3) Oxidation/imation of sulfide. Although oxidation of sulfide to sulfoxide has been reported with 1a in the presence of catalysts, in our system, thioanisole (13) was smoothly converted to the corresponding sulfoxide 14 in high yield under...
catalyst-free conditions. On the other hand, in the presence of N-triflylamine (15), the umpolung product, sulfilimine 16, was exclusively obtained.25 4) **Synthesis of pentavalent \( \lambda^5 \)-bismuthane.** Triphenylbismuth (17) was cleanly oxidized within 10 minutes to give pentavalent \( \lambda^5 \)-bismuthanes (triphenyl(carbonato)bismuth \( \text{Ph}_3\text{BiCO}_3 \) (19) may play a role in this reaction) and after acidic work-up, triphenyl(dichloro)bismuth (18) was obtained in high yield.26,27 5) **Benzyne formation.** The oxidative denitrogenation of 1-aminobenzotriazole (20) with *in-situ*-generated 1a proceeded readily at room temperature to give benzyne adduct 22 in good yield in the presence of a suitable diene 21, as reported for Pb(OAc)$_4$.28

**Scheme 1.** One-pot reactions. Numbers in parentheses are \(^1\)H NMR yields. Conditions: (a) 7 (1 eq), K$_2$CO$_3$ (3 eq), rt, 12 h; (b) 9 (1 eq), K$_2$CO$_3$ (3 eq), rt, 30 min; (c) 11 (0.5 eq), rt, 30 min; (d) 13 (1 eq), rt, 30 min; (e) 13 (1 eq), 14 (1.6 eq), rt, 25 min; (f) 17 (1 eq), rt, 10 min; then 1 M HCl (excess); (g) 20 (1 eq), 21 (1 eq), rt, 30 min.

On the basis of the reported rate acceleration of the disproportionation of NaClO to NaClO$_3$ and NaCl under a CO$_2$ atmosphere,29 together with our Raman spectroscopic study (Figure S1 in the Supporting Information), we consider that the reaction mechanism most likely involves the initial formation of Cl$_2$O or HOCl as an active species (Scheme 2, Figure S2 in the Supporting Information).30 The intervention of Cl$_2$O was further confirmed by connected flask experiment (Figure S3 in the Supporting Information). The disproportionation products, NaClO$_2$ and NaClO$_3$, did not serve as active oxidants (Scheme S1 in the Supporting Information). In an early stage of the oxidation of iodobenzene (4a) (yellow solution stage), we confirmed the presence of PhICl$_2$ 3 and \( \mu \)-oxo dimer 24 by \(^1\)H NMR and ESI-MS analyses (Figure S4 in the Supporting Information). These results suggest that the first step of the oxidation probably involves the nucleophilic attack of iodobenzene on active Cl$^+$ species to give a transient intermediate 23, followed by rapid ligand exchange on the iodine(III) center to give 3 or 24, with the precipitation of polymeric iodosylbenzene (1a). The bands due to I–O stretching vibration of 1a obtained by our method are slightly different from those reported for a sample obtained by NaOH hydrolysis \( (\nu = 490, 445 \text{ cm}^{-1}) \),17 which might suggest differences in the polymeric I–O chain length/angle. The difference in reactivity between 1a prepared by our method and by
the classical hydrolysis method is consistent with this idea (Scheme S2 in Supporting Information). Similar enhancement of the oxidizing ability of iodosylbenzene oligomer [(PhIO)₃SO₃] has been reported by Zhdankin and co-workers.³¹

![Scheme 2. Proposed reaction mechanism.](image)

**Conclusions**

We have developed an efficient method for the preparation of iodosylarene 1 using NaClO and CO₂. Since the method does not require the presence of a base, a variety of subsequent transformations can be performed in one pot. This method should be practically useful in explorations of new areas of organic/organometallic/bioorganic chemistry. Investigations of the reaction mechanism and further applications of NaClO to iodoarene-catalyzed oxidation under CO₂ are in progress.

**Experimental Section**

**General.** IR spectra were recorded on a JASCO FR/IR-4700 spectrometer. Raman spectra were obtained on a NRS-4500 spectrometer. ¹H NMR spectra were recorded on a BRUKER AVANCE III HD 500 spectrometer (TMS, HDO, or CH₂SOCD₃ as an internal standard). GCMS: Mass spectra (MS) were obtained on Agilent 7890A/5975C or 7890B/5977A spectrometers. Electrospray ionization (ESI) mass spectra were recorded on a Shimadzu LC-MS 2020 spectrometer. Melting points were determined in SRS MPA 100 OptiMelt Automated Melting Point System without correction.

Sodium hypochlorite pentahydrate was purchased from Fujifilm Wako Pure Chemical Industries, Co. Ltd. Other materials were purchased from Tokyo Chemical Industry Co., Ltd., Sigma-Aldrich Co., LLC, and Fujifilm Wako Pure Chemical Industries, Co. Ltd.

**CAUTION:** Although we have never encountered any safety-related issues during the synthesis of 1, the product should be stored in a freezer at ≤ –20 °C, since prolonged storage of 1a at room temperature and at 0 °C leads to disproportionation reaction producing a mixture of PhI 4a and potentially explosive PhIO₂ 6a.⁶,³²
Drying under elevated temperature should be avoided, since disproportionation of 1 is known to be accelerated by heating under reduced pressure.\textsuperscript{5,33}

**General procedure for synthesis of PhiO 1a (3 mmol scale).** To a stirred suspension of NaClO-5H\textsubscript{2}O (496 mg, 3.0 mmol) in MeCN (2 mL) was added iodobenzene (4a) (336 µL, 3.0 mmol) under CO\textsubscript{2} at room temperature, and the mixture was vigorously stirred for 10 minutes. To the resulting yellow suspension was added a small amount of water to triturate the solid, which was then was collected by suction filtration. The filter cake was washed with water (3 X 5 mL), then acetone or AcOEt (3 X 5 mL). The product was dried at room temperature under reduced pressure (0.3 Torr) for 2 hours to give 1a (495 mg, 75%) as a pale yellow solid. The purity of 1a was determined by iodometric titration to be 98–100%.

**Iodosylbenzene (1a).**\textsuperscript{17} Mp 191–198 °C (dec); IR (ATR): 3057, 1467, 1439, 991, 725, 525, 446 cm\textsuperscript{-1}.

4-Nitro(iodosyl)benzene (1b). Pale yellow solid; mp 172–193 °C (dec); IR (ATR): 3075, 1600, 1527, 1350, 1308, 1281, 1107, 1040, 1002, 768, 715, 669, 529, 447 cm\textsuperscript{-1}.\textsuperscript{34}

4-(Trifluoromethyl)(iodosyl)benzene (1c). Pale yellow solid; mp 212–215 °C (dec); IR (ATR): 3051, 1594, 1395, 1318, 1130, 1065, 1000, 823, 708, 505, 406 cm\textsuperscript{-1}.\textsuperscript{35}

4-(Methoxycarbonyl)(iodosyl)benzene (1d). Pale yellow solid: 155–187 °C (dec); IR (ATR): 2960, 1717, 1582, 1434, 1390, 1270, 1102, 1002, 849, 738, 675, 534, 471, 418 cm\textsuperscript{-1}.\textsuperscript{20}

4-Chloro(iodosyl)benzene (1e). Pale yellow solid: 160–190 °C (dec); IR (ATR): 3077, 1562, 1466, 1381, 1084, 1001, 803, 769, 713, 517, 473 cm\textsuperscript{-1}.\textsuperscript{20}

4-Methyl(iodosyl)benzene (1f). Pale yellow solid; mp 161–175 °C (dec); IR (ATR): 2917, 1480, 1049, 1005, 792, 766, 714, 475, 447 cm\textsuperscript{-1}.\textsuperscript{12}

2,4,6-Trimethyl(iodosyl)benzene (1g). Pale yellow solid; mp 112.5–113.5 °C (dec); IR (ATR): 2982, 1570, 1456, 1297, 1035, 993, 850, 689, 550–526, 418 cm\textsuperscript{-1}.\textsuperscript{36}

4-Methoxy(iodosyl)benzene (1h). Pale yellow solid. mp 155–165 °C (dec); IR (ATR): 3062, 3007, 2937, 2838, 1568, 1483, 1299, 1243, 1168, 1026, 811, 766, 710, 502, 414 cm\textsuperscript{-1}.\textsuperscript{37}

Iodobenzene (6a): colorless needles; mp 226–228 °C (dec); IR (ATR): 3048, 1567, 1470, 1438, 1047, 995, 757, 706, 677 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (500 MHz, D\textsubscript{2}O): δ 8.04–8.00 (m, 2H), 7.81–7.76 (m, 3H).\textsuperscript{38}

2-Nitro(iodyl)benzene (6b). Pale yellow solid; mp 199–204 °C (dec); IR (ATR): 3084, 3056, 1588, 1523, 1335, 1309, 1105, 856, 793, 769, 755, 735, 472 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (500 MHz, DMSO-d\textsubscript{6}): δ 8.37 (dd, J = 7.9, 1.2 Hz), 8.30 (dd, J = 7.9, 1.2 Hz, 1H), 8.19 (ddd, J = 7.9, 7.6, 1.2 Hz), 7.89 (ddd, J = 7.9, 7.6, 1.2 Hz).\textsuperscript{19}

**Large-scale synthesis of 1a.** To a stirred suspension of NaClO-5H\textsubscript{2}O (13.3 g, 80.8 mmol) in MeCN (40 mL) was added iodobenzene (4a) (15.0 g, 74 mmol) under CO\textsubscript{2} at room temperature, and the mixture was vigorously stirred for 10 minutes. During the reaction, no distinct exothermic event was observed. To the resulting yellow suspension was added a small amount of water to triturate solid, which was then collected by suction filtration. The filter cake was washed with water (10 X 5 mL) until the pH of the filtrate becomes neutral, followed by washing with AcOEt (10 X 5 mL). The resulting pale-yellow solid was dried at room temperature under reduced pressure (0.3 Torr) for 2 hours to give 1a (12.0 g, 74%) as a pale yellow solid. The purity of 1a was determined by iodometric titration to be 94%.

**One-pot synthesis of imino-λ\textsuperscript{3}-iodane 8.** To a stirred suspension of NaClO-5H\textsubscript{2}O (490 mg, 3.0 mmol) in MeCN (2 mL) was added iodobenzene (4a) (335 µL, 3.0 mmol) under CO\textsubscript{2} at room temperature, and the mixture was vigorously stirred for 10 minutes. To the resulting pale-yellow slurry were added 4-nitrobenzenesulfonylamine (7) (606 mg, 3.0 mmol) and K\textsubscript{2}CO\textsubscript{3} (1.24 g, 9.0 mmol) at room temperature, and the mixture was stirred for 12 hours. After the addition of water (ca. 5 mL), the solid was collected by suction filtration. The filter cake was
washed with water (3 X 5 mL) then acetone (3 X 5 mL) to give imino-\(\lambda^3\)-iodane 8 (849 mg, 70%) as a white to pale yellow solid.

\[(\text{N-[4-Nitrophenylsulfonyl]imino}[\text{(phenyl})-\lambda^3\text{-iodane}])\].\(^{39}\) Mp 118–119 °C (dec); \(^1\)H NMR (500 MHz, DMSO-
\(d_6\)): \(\delta\) 8.14–8.00 (m, 2H), 7.82–7.67 (m, 4H), 7.39 (t, \(J = 7.4\) Hz, 1H), 7.25–7.15 (m, 2H).

**One-pot synthesis of iodonium ylide 10.** To a stirred suspension of NaClO-5H\(2\)O (493 mg, 3.0 mmol) in MeCN (2 mL) was added iodobenzene (4a) (335 \(\mu\)L, 3.0 mmol) under \(\text{CO}_2\) at room temperature, and the mixture was vigorously stirred for 10 minutes. To the resulting pale-yellow slurry were added dimedone 9 (420 mg, 3.0 mmol) and \(\text{K}_2\)\(\text{CO}_3\) (1.24 g, 9.0 mmol) at room temperature, and the mixture was stirred for 30 minutes. After addition of dichloromethane (ca. 10 mL), the reaction mixture was filtered. The filtrate was concentrated under reduced pressure to give a white solid, which was recrystallized from dichloromethane-hexane at 4 °C to give iodonium ylide 10 (719 mg, 70%) as colorless prisms.

5,5-Dimethyl-2-(phenyl-\(\lambda^3\)-iodanylidene)cyclohexane-1,3-dione (10).\(^{40}\) Mp 127–129 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.83 (d, \(J = 7.7\) Hz, 2H), 7.52 (t, \(J = 7.5\) Hz, 1H), 7.36 (dd, \(J = 7.7, 7.5\) Hz, 2H), 2.50 (s, 6H). One-pot oxidative deprotection of 1,3-dithiane 11. To a stirred suspension of NaClO-5H\(2\)O (490 mg, 3.0 mmol) in MeCN (2 mL) was added iodobenzene (4a) (335 \(\mu\)L, 3.0 mmol) under \(\text{CO}_2\) at room temperature, and the mixture was vigorously stirred for 10 minutes. To the resulting pale-yellow slurry was added dichloromethane (10 mL) and thioanisole (354 \(\mu\)L, 3.0 mmol) under CO\(_2\) at room temperature, and the mixture was stirred for 30 minutes. The yield of phenyl sulfoxide (15) was 88% as determined by \(^1\)H NMR (mesitylene as an internal standard). Industrially pure 15 was obtained by silica gel column chromatography (hexane only to AcOEt only) as a colorless oil.

Methyl phenyl sulfoxide (15).\(^{42}\) \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.68–7.63 (m, 2H), 7.58–7.48 (m, 3H), 2.74 (s, 3H). MS: \(m/z\) (relative intensity): 140 (\(M^+\), 74%), 125 (100), 124 (47), 77 (51).

One-pot oxidative amination of thioanisole 13. To a stirred suspension of NaClO-5H\(2\)O (492 mg, 3.0 mmol) in MeCN (2 mL) was added iodobenzene (4a) (335 \(\mu\)L, 3.0 mmol) under \(\text{CO}_2\) at room temperature, and the mixture was vigorously stirred for 10 minutes. To the resulting pale-yellow slurry were added triflylamide 14 (715 mg, 4.8 mmol) and thioanisole 13 (354 \(\mu\)L, 3.0 mmol), and the mixture was stirred for 25 minutes. The yield of sulfilimine 16 was 78% and that of sulfone 15 was 16%, as determined by \(^1\)H NMR (mesitylene as an internal standard). The solvent was removed under reduced pressure, and the resulting pale yellow oil was recrystallized from dichloromethane-hexane at 4 °C to give analytically pure 16 (529 mg, 65%) as colorless plates.

S-Methyl-S-phenyl-N-(trifluoromethanesulfonyl)sulfilimine (16).\(^{43}\) Mp 117–118 °C; \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.84 (d, \(J = 8.4\) Hz, 2H), 7.72–7.60 (m, 3H), 3.02 (s, 3H); \(^{19}\)F NMR (470 MHz, CDCl\(_3\)): \(\delta\) -78.9 ppm (s, 3F).

One-pot synthesis of triphenyl(dichloro-\(\lambda^3\)-bismuthane 18. To a stirred suspension of NaClO-5H\(2\)O (493 mg, 3.0 mmol) in MeCN (2 mL) was added iodobenzene (4a) (335 \(\mu\)L, 3.0 mmol) under \(\text{CO}_2\) at room temperature, and the mixture was vigorously stirred for 10 minutes. To the resulting pale-yellow slurry was added triphenylbismuth 17 (1.32 g, 3.0 mmol), and the mixture was stirred for 10 minutes. After addition of 1 M aqueous HCl solution (10 mL), the resulting white solid was collected by suction filtration. The filter cake was washed with water (3 X 5 mL), then hexane (3 X 5 mL). The solid was dried under reduced pressure (0.3 Torr)
for 2 hours, followed by recrystallization from dichloromethane-hexane at room temperature to give analytically pure triphenyl(dichloro)-λ⁵-bismuthane (18) (1.1 g, 72%) as colorless prisms. **Triphenyl(dichloro)-λ⁵-bismuthane (18).** Mp 158–162 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.53 (d, J = 8.3 Hz, 6H), 7.66 (dd, J = 8.3, 7.4 Hz, 6H), 7.54 (t, J = 7.4 Hz, 3H).

**One-pot generation of benzyne with 1-aminobenzotriazole 20.** To a stirred suspension of NaClO·5H₂O (67.6 mg, 0.41 mmol) in MeCN (230 µL) was added iodobenzene (4a) (45.8 µL, 0.41 mmol) under CO₂ at room temperature, and the mixture was vigorously stirred for 10 minutes. To the resulting pale-yellow slurry were added MeCN (1.0 mL), 2,3,4,5-tetraphenylcyclopenta-2,4-dien-1-one (21) (158 mg, 0.41 mmol), and 1-aminobenzotriazole (20) (55.1 mg, 0.41 mmol), and the mixture was stirred for 30 minutes. The yield of benzyne adduct 22 was 75%, as determined by ¹H NMR (1,1,2,2-tetrachloroethane as an internal standard). The solvent was removed under reduced pressure, and the resulting oil was purified by silica gel column chromatography (hexane : CHCl₃ = 77 : 23 to 75 : 25) to give 1,2,3,4-tetraphenylnaphthalene (120 mg, 68%) as a white solid.

**1,2,3,4-Tetraphenylnaphthalene (22).** ¹H NMR (500 MHz, CDCl₃): δ 7.64 (dd, J = 6.4, 3.1 Hz, 2H), 7.39 (dd, J = 6.4, 3.1 Hz, 2H), 7.27–7.15 (m, 10H), 6.88–6.78 (m, 10H).

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**Supplementary Material**

Supplementary data (Scheme S1, Scheme S2, Figure S1, and Figure S2) associated with this article can be found, in the online version, at URL: https...

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