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CO_2-activated NaClO-$5H_2O$ enabled smooth oxygen transfer to iodoarene: a highly practical synthesis of iodosylarene

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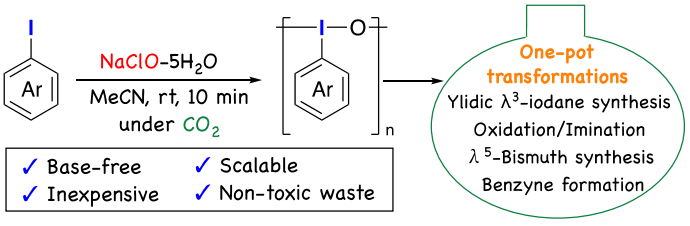
We wish to dedicate this paper to the memory of Professor Kilian Muñiz, who devoted his life to the development of hypervalent iodine chemistry

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Abstract

A safe, rapid, and environmentally friendly synthesis of iodosylarene (ArIO) has been developed using NaClO under a carbon dioxide (CO_2) atmosphere. Exposure of iodoarene to NaClO-$5H_2O$ in acetonitrile under CO_2 (1 atm) resulted in the clean formation of ArIO 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, benzyne adduct, etc.), but also for the synthesis of iodonium ylide and imino-λ^3-iodane in one pot.



Keywords: Iodosylbenzene; sodium hypochlorite; carbon dioxide; imino-λ^3-iodane; iodonium ylide; oxidation; benzyne

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Introduction

Hypervalent iodine(III) reagents (aryl-λ^3-iodane with two heteroatom ligands) have enjoyed widespread use in modern organic synthesis as a potent, safe, and environmentally friendly oxidant.[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 $L_nM{=}O$, which are present in the active center of many oxidases, and 3) **versatility as a precursor** not only for aryl-λ^3-iodanes with heteroatom ligands (F, OH, OR, OAc, $OCOCF_3$, OTs, NSO_2R, etc.), but also for aryl-λ^3-iodanes with carbon ligands (aryl, vinyl, alkynyl, methylide, etc.).[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).[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.[12] This is problematic, because **1a** is light-sensitive and gradually decomposes at room temperature.[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**).[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 $NaClO{\cdot}5H_2O$ with carbon dioxide (CO_2).

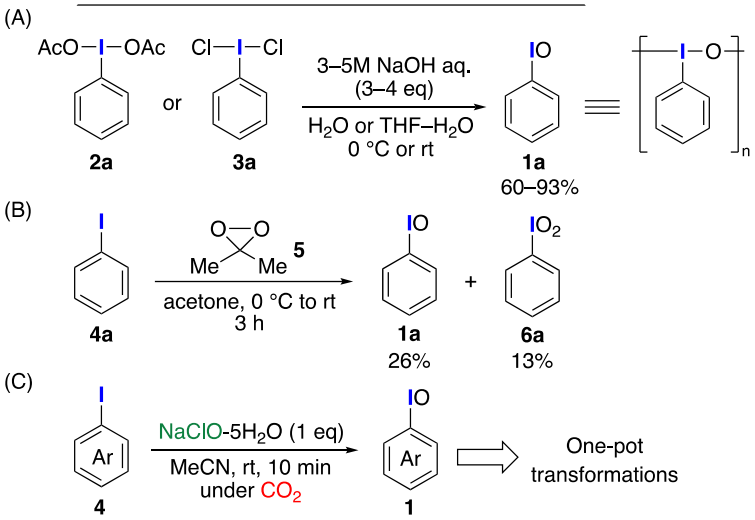


Figure 1. Approaches for the synthesis of **1**. (A) Typical alkaline hydrolysis approach. (B) Direct oxidation approach. (C) Present approach.

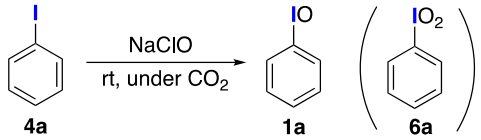
Results and Discussion

We recently reported that $NaClO{\cdot}5H_2O$ serves as an excellent oxidant for the synthesis of (diacetoxyiodo)arene **2** in the presence of acetic acid at room temperature.[14] We also reported that the oxidation of 2-iodobenzoic acid **7** with $NaClO{\cdot}5H_2O$, leading to the formation of 2-iodoxybenzoic acid (IBX) **8**, is accelerated by gaseous CO_2.[15,16] Encouraged by these findings, we commenced our study by examining the direct oxidation of iodobenzene (**4a**) with $NaClO{\cdot}5H_2O$ under a CO_2 atmosphere. Exposure of **4a** to equimolar $NaClO{\cdot}5H_2O$ in MeCN at room temperature under CO_2 (1 atm) resulted in the rapid appearance (within a few

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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^{-1}).[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 CO_2 (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, CH_2Cl_2, 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).[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 $PhIO_2$ **6a**, instead of **1a** (entries 12–14).[14,15] In contrast, $Ca(ClO)_2$-$3H_2O$ did not work at all in this system, partly because of its poor solubility in MeCN (entry 15). The substitution of CO_2 with solid $NaHCO_3$ is potentially attractive in terms of convenience and cost, though the yield of **1a** is only moderate (entry 15).

Table 1. Oxidation of iodobenzene **4a** with NaClO under CO_2.



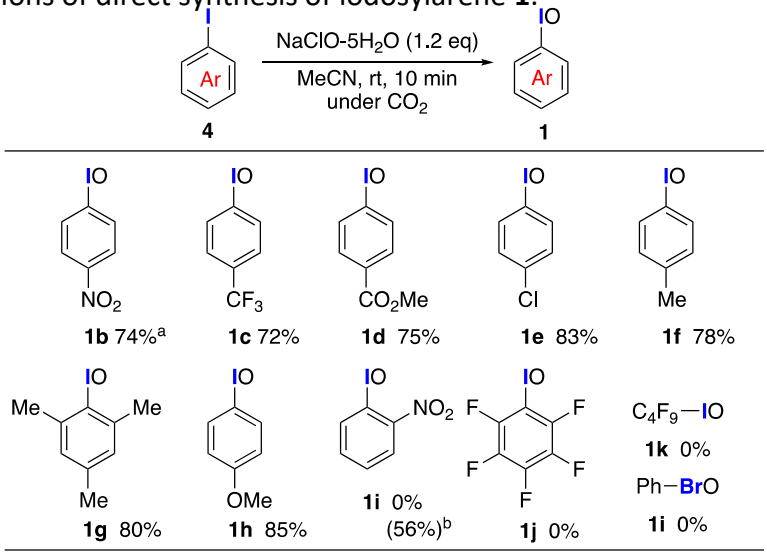
entry	ClO^- source (equiv)	solvent	time	yield (%)[a]
1	NaClO-$5H_2O$ (1.0)	MeCN	10 min	75–78 (3 runs)
2[b]	NaClO-$5H_2O$ (1.0)	MeCN	2 h	0
3	NaClO-$5H_2O$ (1.0)	MeCN	10 min	78 (20 mmol)
4	NaClO-$5H_2O$ (1.1)	MeCN	10 min	74 (74 mmol)
5	NaClO-$5H_2O$ (1.0)	–	3 h	13
6	NaClO-$5H_2O$ (1.0)	PhMe	12 h	0
7	NaClO-$5H_2O$ (1.0)	CH_2Cl_2	12 h	13
8	NaClO-$5H_2O$ (1.0)	AcOEt	24 h	32
9	NaClO-$5H_2O$ (1.0)	acetone	20 min	0[c]
10	NaClO-$5H_2O$ (1.0)	DMF	20 min	0[c]
11	NaClO-$5H_2O$ (1.0)	THF	20 min	0[c]
12	4% NaClO (1.1)	MeCN	60 min	45
13	13% NaClO (1.1)	MeCN	30 min	72
14	13% NaClO (2.8)	MeCN	30 min	0[d]
15	$Ca(ClO)_2$-$3H_2O$ (0.5)	MeCN	30 min	0
16[b,e]	NaClO-$5H_2O$ (1.1)	MeCN	2 h	51

Unless otherwise noted, reactions were performed on 2.5–3 mmol scale in MeCN (1.5 M) under CO_2 (1 atm). [a]Isolated yields. [b]Under air. [c]Decomposition of NaClO-$5H_2O$ occurred within 10 minutes. [d]$PhIO_2$ **6a** (89%, based on oxidant used) was obtained. [e]$NaHCO_3$ (1.1 eq) was used instead of CO_2.

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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.[19] 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.[20] The attempted oxidation of highly electron-deficient pentafluoroiodobenzene (**4j**) was unsuccessful, in marked contrast to the facile oxidation of **4j** in AcOH, yielding $C_6F_5I(OAc)_2$.[14] Other electron-deficient substrates, (nonafluorobutyl iodide (**4k**) and bromobenzene (**4i**)), were not oxidized under these conditions.

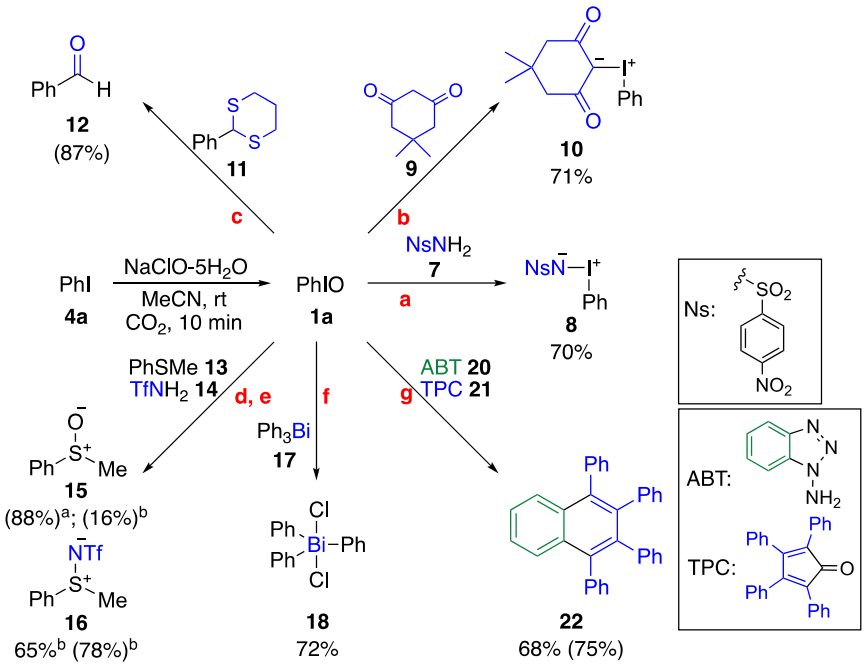
Table 2. Scope and limitations of direct synthesis of iodosylarene **1**.



All reactions were performed on 3 mmol scale in MeCN (1.5 M) under CO_2 (1 atm). [a]30 min. [b]Yield of 2-nitro(iodyl)benzene (**6b**) based on the $NaClO\text{-}5H_2O$ used.

Gratifyingly, the base-free preparation of **1a** enabled a variety of one-pot transformations (Scheme 1), as follows. **1) Direct synthesis** of ylidic λ^3-iodanes.[21,22] In the presence of K_2CO_3, 4-nitrobenzenesulfonamide (**7**) and dimedone (**9**) underwent ligand exchange and afforded synthetically useful imino-λ^3-iodane **8** and iodonium ylide **10**, respectively, in good yields. **2) Rapid deprotection of dithioacetal**. Oxidative hydrolysis of dithioacetal **11** with in-situ-formed **1a** proceeded at room temperature within 30 minutes to give benzaldehyde (**12**) in high yield.[23] 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/imination of sulfide**. Although oxidation of sulfide to sulfoxide has been reported with **1a** in the presence of catalysts,[24] 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*-triflylamide (**15**), the umpolung product, sulfilimine **16**, was exclusively obtained.[25] **4) Synthesis of pentavalent λ^5-bismuthane**. Triphenylbismuth (**17**) was cleanly oxidized within 10 minutes to give pentavalent λ^5-bismuthanes (triphenyl(carbonato)bismuth Ph_3BiCO_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]

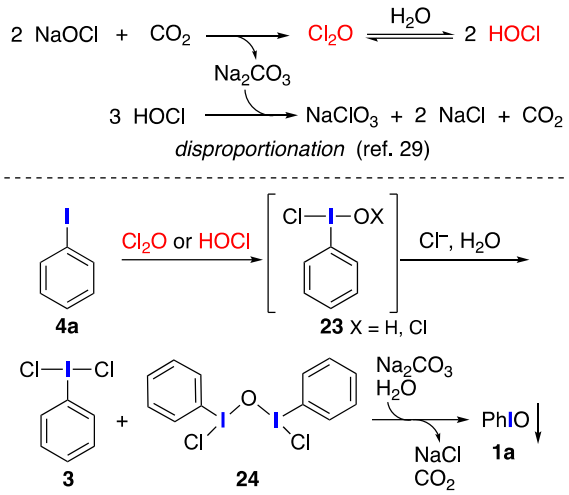
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Scheme 1. One-pot reactions. Numbers in parentheses are ^{1}H NMR yields. Conditions: (a) **7** (1 eq), K_2CO_3 (3 eq), rt, 12 h; (b) **9** (1 eq), K_2CO_3 (3 eq), rt, 30 min; (c) **11** (0.5 eq), rt, 30 min; (d) **13** (1 eq), rt, 30 min; (e) **13** (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. [a]Yield without **14**. [b]Yield with **14**.

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_2O or HOCl as an active species (Scheme 2, Figure S2 in the Supporting Information).[30] The intervention of Cl_2O 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 μ-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 (ν = 490, 445 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 $[(PhIO)_3SO_3]$ has been reported by Zhdankin and co-workers.[31]

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Scheme 2. Proposed reaction mechanism.

Conclusions

We have developed an efficient method for the preparation of iodosylarene **1** using NaClO and CO_2. 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 CO_2 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. ^{1}H NMR spectra were recorded on a BRUKER AVANCE III HD 500 spectrometer (TMS, HDO, or CHD_2SOCD_3 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 **1** at room temperature and at 0 °C leads to disproportionation reaction producing a mixture of PhI **4a** and potentially explosive $PhIO_2$ **6a**.[6,32] Drying under elevated temperature should be avoided, since disproportionation of **1** is known to be accelerated by heating under reduced pressure.[5,33]

General procedure for synthesis of PhIO 1a (3 mmol scale). To a stirred suspension of NaClO-$5H_2O$ (496 mg, 3.0 mmol) in MeCN (2 mL) was added iodobenzene (**4a**) (336 µL, 3.0 mmol) under CO_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

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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).[17] Mp 191–198 °C (dec); IR (ATR): 3057, 1467, 1439, 991, 725, 525, 446 cm^{-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^{-1}.[34]

4-(Trifluromethyl)(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^{-1}.[35]

4-(Methoxycarbonyl)iodosylbenzene (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^{-1}.[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^{-1}.[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^{-1}.[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^{-1}.[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^{-1}.[37]

Iodylbenzene (6a): colorless needles; mp 226–228 °C (dec); IR (ATR): 3048, 1567, 1470, 1438, 1047, 995, 757, 706, 677 cm^{-1}; ^{1}H NMR (500 MHz, D_2O): δ 8.04–8.00 (m, 2H), 7.81–7.76 (m, 3H).[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^{-1}; ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.37 (dd, *J* = 7.9, 1.2 Hz, 1H), 8.30 (dd, *J* = 7.9, 1.2 Hz, 1H), 8.19 (ddd, *J* = 7.9, 7.6, 1.2 Hz), 7.89 (ddd, 7.9, 7.6, 1.2 Hz).[19]

Large-scale synthesis of 1a. To a stirred suspension of NaClO-5H_2O (13.3 g, 80.8 mmol) in MeCN (40 mL) was added iodobenzene (**4a**) (15.0 g, 74 mmol) under CO_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 was 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^3-iodane 8. To a stirred suspension of NaClO-5H_2O (490 mg, 3.0 mmol) in MeCN (2 mL) was added iodobenzene (**4a**) (335 µL, 3.0 mmol) under CO_2 at room temperature, and the mixture was vigorously stirred for 10 minutes. To the resulting pale-yellow slurry were added 4-nitrobenzenesulfonamide (**7**) (606 mg, 3.0 mmol) and K_2CO_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-λ^3-iodane **8** (849 mg, 70%) as a white to pale yellow solid.

[*N*-(4-Nitrophenylsulfonyl)imino](phenyl)-λ^3-iodane (8).[39] Mp 118–119 °C (dec); ^{1}H NMR (500 MHz, DMSO-d_6): δ 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_2O (493 mg, 3.0 mmol) in MeCN (2 mL) was added iodobenzene (**4a**) (335 µL, 3.0 mmol) under CO_2 at room temperature, and the mixture was

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vigorously stirred for 10 minutes. To the resulting pale-yellow slurry were added dimedone **9** (420 mg, 3.0 mmol) and K_2CO_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-λ³-iodanylidene)cyclohexane-1,3-dione (10).[40] Mp 127–129 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 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, 4H), 1.07 (s, 6H).

One-pot oxidative deprotection of 1,3-dithiane 11. To a stirred suspension of NaClO-$5H_2O$ (490 mg, 3.0 mmol) in MeCN (2 mL) was added iodobenzene (**4a**) (335 µL, 3.0 mmol) under CO_2 at room temperature, and the mixture was vigorously stirred for 10 minutes. To the resulting pale-yellow slurry was added 1,3-dithiane **11** (294 mg, 1.5 mmol) at room temperature, and the mixture was stirred for 30 minutes. The yield of benzaldehyde (**12**) was 87% as determined by ^{1}H NMR (mesitylene as an internal standard).

Benzaldehyde (12).[41] ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.03 (s, 1H), 7.89 (d, *J* = 7.9 Hz, 2H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.54 (dd, *J* = 7.9, 7.5 Hz, 2H). MS: *m/z* (relative intensity): 106 (M^+, 86%), 105 (100), 77 (94).

One-pot oxidation of thioanisole 13. To a stirred suspension of NaClO-$5H_2O$ (492 mg, 3.0 mmol) in MeCN (2 mL) was added iodobenzene (**4a**) (335 µL, 3.0 mmol) under CO_2 at room temperature, and the mixture was vigorously stirred for 10 minutes. To the resulting pale-yellow slurry were added dichloromethane (10 mL) and thioanisole **13** (354 µL, 3.0 mmol), and the mixture was stirred for 30 minutes. The yield of methyl phenyl sulfoxide (**15**) was 88% as determined by ^{1}H NMR (mesitylene as an internal standard). Analytically 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, $CDCl_3$): δ 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-$5H_2O$ (489 mg, 3.0 mmol) in MeCN (2 mL) was added iodobenzene (**4a**) (335 µL, 3.0 mmol) under 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** (350 µL, 3.0 mmol), and the mixture was stirred for 25 minutes. The yield of sulfilimine **16** was 78% and that of sulfoxide **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, $CDCl_3$): δ 7.84 (d, *J* = 8.4 Hz, 2H), 7.72–7.60 (m, 3H), 3.02 (s, 3H); ^{19}F NMR (470 MHz, $CDCl_3$): δ -78.9 ppm (s, 3F).

One-pot synthesis of triphenyl(dichloro)-λ⁵-bismuthane 18. To a stirred suspension of NaClO-$5H_2O$ (493 mg, 3.0 mmol) in MeCN (2 mL) was added iodobenzene (**4a**) (335 µL, 3.0 mmol) under 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)-λ^5-bismuthane (**18**) (1.1 g, 72%) as colorless prisms.

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Triphenyl(dichloro)-λ^5-bismuthane (18).[44] Mp 158–162 °C; ^{1}H NMR (500 MHz, $CDCl_3$): 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-5H_2O (67.6 mg, 0.41 mmol) in MeCN (230 µL) was added iodobenzene (**4a**) (45.8 µL, 0.41 mmol) under CO_2 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 ^{1}H 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 : $CHCl_3$ = 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).[45] ^{1}H NMR (500 MHz, $CDCl_3$): 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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