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Single-Electron-Transfer (SET)-Induced Oxidative Biaryl Coupling by Polyalkoxybenzene-Derived Diaryliodonium(III) Salts

Nobutaka Yamaoka, Kohei Sumida, Itsuki Itani, Hiroko Kubo, Yusuke Ohnishi, Sho Sekiguchi, Toshifumi Dohi, and Yasuyuki Kita*[a]

Abstract: Metal-free oxidative C–C coupling by using polyalkoxybenzene-derived diaryliodonium(III) salts as both the oxidant and aryl source has been developed. These salts can induce single-electron-transfer (SET) oxidation to yield electron-rich arenes and subsequently transfer the polyalkoxyphenyl group into in situ generated aromatic radical cations to produce biaryl products. The reaction is promoted by a Lewis acid that activates the iodonium salts. It has been revealed that the reactivity of the salts under acidic conditions is quite different to their known behavior under basic conditions. The reactivity preference of a series of iodonium salts in the SET oxidation and their ligand transfer abilities have been systematically investigated and the results are summarized in this report.

Keywords: biaryls • cross coupling • hypervalent compound • iodine • radical ions • umpolung

Introduction

Diaryliodonium(III) salts (Figure 1), in which the iodine atom adopts a T-shaped form with two bound aryl moieties and a ligand (X), have been used in organic synthesis as versatile arylating agents and benzyne precursors as well as for other applications, such as active bactericides and photoacid generators (PAG) for cationic polymerization processes.[1] These compounds are generally air- and moisture-stable, and in recent years some research groups have successfully developed convenient synthetic routes to diaryliodonium salts from nonfunctionalized arenes and hypervalent iodine reagents or iodoarenes in combination with appropriate oxidants.[2]

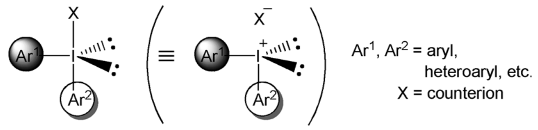
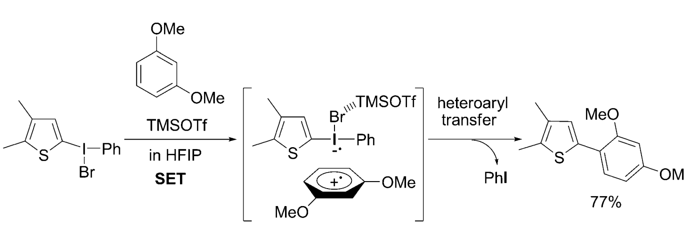


Figure 1. Structural description of diaryliodonium(III) salts.

By taking advantage of the excellent leaving ability as more stable monovalent iodoarene moieties, nucleophilic substitution reactions with organometallic reagents or enolates under basic conditions[3] as well as transition-metal-catalyzed coupling reactions[4] have been developed by using iodonium salts in chemical reactions. These reactions rarely proceed except under basic conditions by activation with a transition-metal catalyst and/or at high temperature.[5] Hence the reactivities of diaryliodonium salts as arylating agents under acidic conditions have rarely been reported to date.

Our research group has recently become interested in the chemical behavior of diaryliodonium salts under acidic conditions. During our investigations we have discovered that unprecedented metal-free oxidative coupling reactions occur under acidic conditions with in situ formed diaryliodonium salts of heteroaromatic compounds as the key intermediates.[6a] Later, regioselective dimerization reactions to produce head-to-tail bithiophenes were also accomplished by this strategy.[6b–d] In these studies we unexpectedly discovered the single-electron-transfer (SET) oxidizing ability of heteroaryliodonium bromides through the activation of trimethylsilyl triflate (TMSOTf) during cross-coupling reactions with electron-rich arenes and heteroaromatic compounds under metal-free conditions (Scheme 1).[7]

Regarding the SET oxidizing ability of a hypervalent iodine reagent, our research group first discovered in the early 1990s that various nucleophiles can be introduced into



Scheme 1. *ipso*-Substitution of thienyliodonium bromides under acidic conditions. HFIP = 1,1,1,3,3,3-hexafluoroisopropanol.

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[a] N. Yamaoka, K. Sumida, I. Itani, H. Kubo, Y. Ohnishi, S. Sekiguchi, Dr. T. Dohi, Prof. Dr. Y. Kita
College of Pharmaceutical Sciences, Ritsumeikan University
1-1-1 Nojihigashi, Kusatsu, Shiga 525-8577 (Japan)
Fax: (+81) 77-561-5829
E-mail: kita@ph.ritsumei.ac.jp

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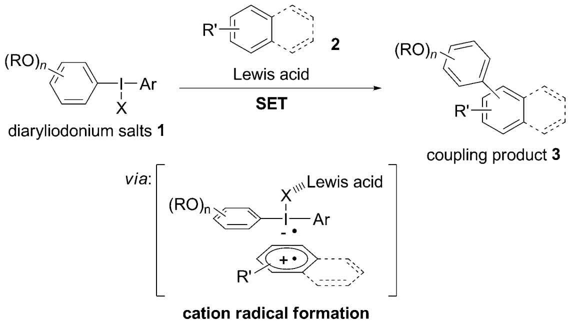
phenyl ethers by the SET oxidation of the aromatic rings induced by phenyliodine(III) bis(trifluoroacetate) (PIFA).[8a,b] By using this unique umpolung aromatic ring strategy, a series of metal-free couplings of nucleophiles[8] as well as biaryl couplings[9] were achieved with various electron-rich aromatic compounds in specific solvents and/or in combination with Lewis acids. Encouraged by these results, SET oxidation reactions with other hypervalent iodine reagents, for example, [hydroxy(tosyloxy)iodo]benzene (HTIB, Koser's reagent), were also recently proposed.[10] On the other hand, the SET oxidizing ability of diaryliodonium salts has never been investigated. Our newly discovered coupling of heteroaryl-containing diaryliodonium salts is the first and only example revealing the unprecedented SET oxidation ability of the salts.[7]

Nonetheless, it is still unclear whether diaryliodonium salts containing non-heteroaryl groups can induce the SET oxidation of aromatic compounds. Therefore we were interested in investigating the SET oxidizing ability of an extensive series of diaryliodonium salts in the metal-free coupling of aromatic compounds. To this objective, we now report our study on the SET oxidation reactions with diaryliodonium salts derived from polyalkoxybenzenes instead of heteroaryls as the aryl ligand on the iodine atom (Scheme 2).

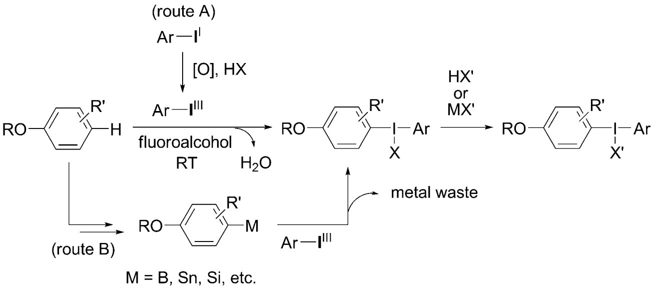


Scheme 2. New coupling reaction based on the SET mechanism initiated by polyalkoxybenzene-derived diaryliodonium salts **1**.

The reactivities of these salts in the SET oxidation reactions with Lewis acids and the subsequent ligand transfer into the generated aromatic radical cations to produce oxidatively coupled substrates have been investigated in detail.

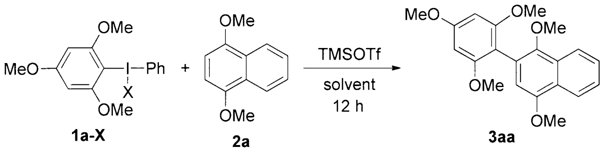
Results and Discussion

Biaryl coupling reactions of aromatic compounds by using polyalkoxybenzene-derived diaryliodonium(III) salts by the SET oxidation pathway: In our previous work, the presence of electron-rich heteroaryl groups in the thienyliodonium(III) bromides was crucial for initiating the coupling reactions, electron-deficient salts showing no reaction.[7] We thus speculated on the reactivity of diaryliodonium salts **1** derived from electron-rich alkoxybenzenes. Conventional synthetic approaches to these iodonium salts **1** by the metal functionalization of aromatic rings have been reported,[11] but this led to the production of a large amount of waste material (Scheme 3, stepwise route B). On the other hand, we have recently developed a direct dehydrative approach towards various diaryliodonium salts with polyalkoxybenzenes as the starting substrates in fluoroalcohols as solvent,[12] and in a greener strategy, the corresponding iodonium salts **1** were readily prepared without the prefunctionalization of arenes (Scheme 3, direct route A). The use of fluoroalcohols can enhance the oxidation of iodine to its trivalent form,[13] and thus the preparation of iodonium salts from aryl iodides by not using a hypervalent iodine compound was also possible.[12e] The counter ions, X, can be easily exchanged by treating with the required acids or inorganic salts after the preparations.[11f]



Scheme 3. General approaches for to the preparation of alkoxybenzene-derived diaryliodonium salts **1**.

With these diaryliodonium salts **1** in hand, relying on our previous reaction system,[7] we first examined the iodonium bromide **1a-Br** (X = Br), derived from 1,3,5-trimethoxybenzene in the presence of TMSOTf (2 equiv), in the coupling reaction with 1,4-dimethoxynaphthalene (**2a**, 1.5 equiv) in hexafluoroisopropanol (HFIP) as solvent at room temperature [Eq. (1)].



(1)

However, the reaction barely proceeded under these conditions (14% formation of the product **3aa**), and the salts **1a-X** with other counter ions, for example, Cl, BF_4, and OTf, also gave poor results, producing only the coupling product **3aa** in low yields with HFIP as solvent (up to 45%). Therefore we needed to optimize the reaction conditions for the salt **1a** (Table 1). Although HFIP was not a suitable solvent for the reaction of the alkoxybenzene-derived iodonium salt **1a-X**, the less polar fluoroalcohol, 2,2,2-trifluroethanol (TFE), led to slight improvements in the yields of **3aa** for all the salts **1a-X** with different counter ions (Table 1, entries 1–4). These two fluoroalcohols, HFIP

Table 1. Screening of solvents and counterions in the coupling reaction in Equation (1).[a]

Entry	Counter ion (X)	Solvent	Temperature	Yield [%][b]
1	Br	TFE	RT	30
2	Cl	TFE	RT	67
3	BF_4	TFE	RT	43
4	OTf	TFE[c]	RT	69
5	Br	CH_2Cl_2	0 °C–RT	39
6	Cl	CH_2Cl_2	0 °C–RT	77
7	BF_4	CH_2Cl_2	0 °C–RT	74
8	OTf	CH_2Cl_2	0 °C–RT	85

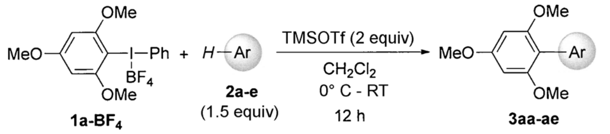
[a] Reagents and conditions: diaryliodonium salt **1a-X** (1 equiv), 1,4-dimethoxynaphthalene (**2a**, 1.5 equiv), TMSOTf (2 equiv), solvent (0.1 M for the salt **1a-X**), 12 h, 0 °C–RT. [b] Isolated yield after purification. [c] TFE = 2,2,2-trifluoroethanol (CF_3CH_2OH).

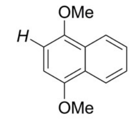
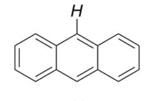
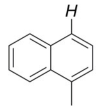
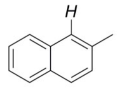
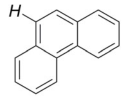
and TFE, are highly polar solvents exhibiting the empirical polarity parameters $E_T(30) = 69.3$ and 59.5, respectively.[14] Because the neutral λ^3 form of the iodonium salts **1** exists in equilibrium with an ionized species in solution, as shown in Figure 1, depending on the solvent,[15] it appears in polar media that the salts **1** are in general fully dissociated or at least present in the ionized form, which seems to render the salts **1a-X** less reactive during the reaction as a result of solvation. Accordingly, the use of nonpolar dichloromethane as solvent was examined. The reaction was conducted between 0 °C and ambient temperature and, fortunately, the reaction proceeded more readily to give the coupling product **3aa** in higher yields (entries 5–8) than was achieved in the fluoro alcohols. The iodonium salts with the counter ions Cl, BF_4, and OTf gave acceptable yields of the product **3aa**, whereas **1a-Br** with a bromo group was less effective due to the instability of this salt relative to the others.

Further optimization of the Lewis acid promoter by using the iodonium triflate **1a-OTf** in dichloromethane revealed that other silicon- and boron-based Lewis acids, that is, trimethylsilyl chloride (TMSCl) and boron trifluoride ($BF_3{\cdot}Et_2O$), and even Brønsted acids, for example, trifluoroacetic acid, were all effective for this reaction (78–83 %).

Based on the optimized conditions for the salt **1a-BF$_4$**, we then sought to investigate the scope and limitation of the coupling partners **2**. According to our hypothesis, the diaryliodonium salts **1** would induce a one-electron oxidation of the electron-rich arene **2a** to generate the corresponding aromatic radical cation species, and thus we explored the relationship between the oxidation potential of the aromatic compounds **2** and the yields of the coupling products **3** (Table 2). Electron-rich arenes **2** with low oxidation potentials (ca. 1.10 V (vs SCE)), 1,4-dimethoxynaphthalene (**2a**) and anthracene (**2b**),[16a] readily reacted to give **3aa** and **3ab** in yields of 74 and 65 %, respectively. On the other hand, compounds **2** with much higher oxidation potentials were less effective coupling partners, and lower yields were observed in their reactions, especially for substrates **2c–e**, which have oxidation potentials greater than 1.5 V. Although the salt **1a-BF$_4$** was still reactive towards the aromatic compounds **2c** and **2d** ($E^{ox} = 1.59$–1.64 V),[16b] phenanthrene (**2e**), which is more difficult to oxidize ($E^{ox} = 1.83$ V),[16c] did not react at all and was recovered unreacted. These results indicate that the salts **1a** react with arenes **2** with a range of oxidation potentials below 1.65 V.

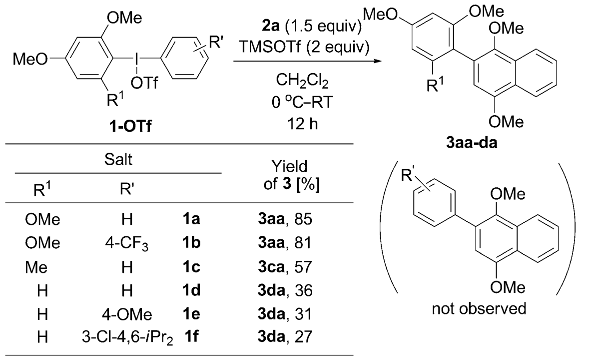
Table 2. Relationship between the reactivity and oxidation potential of the aromatic compounds **2**.[a]



Entry	Ar-*H* (**2**)	E^{ox} [V] (vs. SCE)[b]	Product **3**	Coupling yield [%][c]
1	 **2a**	1.10	**3aa**	74
2	 **2b**	1.09	**3ab**	65
3	 **2c**	1.59	**3ac**	31
4	 **2d**	1.64	**3ad**	45[d]
5	 **2e**	1.83	**3ae**	trace

[a] Reagents and conditions: salt **1a-BF$_4$** (1 equiv), arene **2** (1.5 equiv), TMSOTf (2 equiv), CH_2Cl_2 (0.1 M relative to the salt), 12 h, 0 °C–RT. [b] For Ar-H **2**, see ref. [16] for the reported values. [c] Isolated yield. [d] Formation of a very small amount of regioisomer was observed.

We then examined the reactivity of derivatives of the diaryliodonium salt **1a**. As shown in Scheme 4, the salts **1a-OTf** and **1b-OTf** derived from 1,3,5-trimethoxybenzene gave the coupling product **3aa** in excellent yields regardless of the presence of the 4-CF$_3$ aryl group in **1b-OTf**. Interestingly, in the latter case, only the electron-rich 1,3,5-trime-

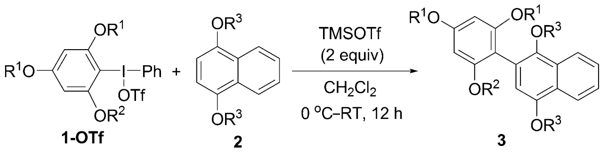


Salt			Yield of **3** [%]
R^1	R'		
OMe	H	**1a**	**3aa**, 85
OMe	4-CF$_3$	**1b**	**3aa**, 81
Me	H	**1c**	**3ca**, 57
H	H	**1d**	**3da**, 36
H	4-OMe	**1e**	**3da**, 31
H	3-Cl-4,6-*i*Pr$_2$	**1f**	**3da**, 27

Scheme 4. Reactivity of diaryliodonium salt derivatives **1a–f**. Reagents and conditions: iodonium salt **1-OTf** (1 equiv), 1,4-dimethoxynaphthalene (**2a**, 1.5 equiv), TMSOTf (2 equiv). CH_2Cl_2 at 0 °C–RT for 12 h (see Table 1).

thoxybenzene moiety coupled with the partner **2a**, whereas the other electron-poor aromatic ring with a trifluoromethyl group, which preferentially reacts with nucleophiles under basic conditions,[17] did not participate in the coupling reaction under our acidic conditions. When one of the methoxy substituents was replaced by a methyl group, salt **1c**, the coupling yield decreased to 57%. When one of the methoxy substituents was replaced by a hydrogen, salt **1d**, the yield was even lower, and the presence of a methoxy group on the other aromatic ring, iodonium salt **1e**, did not significantly affect the reactivity. In brief, the substituent on the other aromatic ring (R′) was not influential in the coupling selectivities of the polyalkoxybenzenes. Importantly, the well-known "*ortho* effect" rule for anticipating the reactivity of diaryliodonium salts under basic conditions[18] was totally invalid for these coupling reactions under acidic conditions. Thus, the exclusive reaction of the dimethoxyphenyl group of the iodonium salt **1f** to produce **3da** was observed and not the reaction of the bulkier 4,6-diisopropylaryl group as predicted by the "*ortho* effect". These results clearly show that the presence of the electron-rich aryl moieties in the iodonium salts **1** is crucial for inducing the coupling reactions.

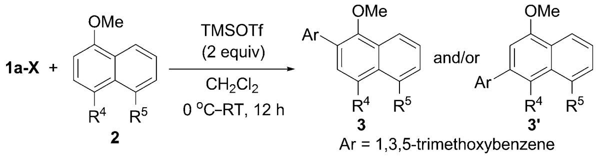
Encouraged by these outcomes, we surveyed the coupling reactions of a range of diaryliodonium triflates **1-OTf** and electron-rich naphthalenes **2** bearing functional groups. Representative results are presented in Scheme 5. The diaryliodonium salt **1g** bearing other alkoxy moieties, for example, an ethoxy group, also showed good reactivity. The functionalized salt **1h** led to *ipso* substitution at the carbon bound to the iodine to selectively provide the product **3ha** in which the naphthalene **1a** is linked to the *ortho* position of the cyanoalkoxy functionality. Meanwhile, the naphthalene **2f** bearing the bulkier isobutyl substituent, was also reactive in the coupling reaction with salt **1a**, the corresponding product **3af** being obtained in high yield.



Salt			Naphthalene		Yield of 3 [%]
R1	R2		R3		
Et	Et	**1g**	Me	**2a**	**3ga**, 63
Me	CH_2CN	**1h**	Me	**2a**	**3ha**, 93[a]
Me	Me	**1a**	*i*Bu	**2f**	**3af**, 79

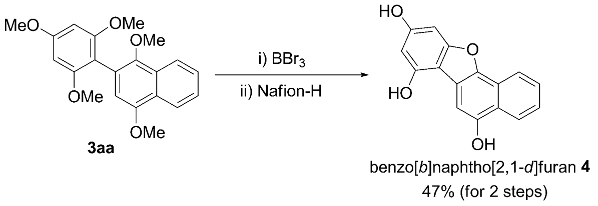
Scheme 5. Reactivity of diaryliodonium salt derivatives. Reagents and conditions: iodonium salt **1-X** (1 equiv), electron-rich naphthalene **2** (1.5 equiv) under the optimized conditions. [a] The formation of very small amount of a regioisomer was detected.

Next we examined the reactions with unsymmetrical naphthalenes **2g–l** to investigate the regioselectivity of the reaction (Scheme 6). The regioselectivity was not biased by the introduction of a bulky alkoxy moiety (R^4), the products **3ag** and **3′ag** being quantitatively obtained from the naphthalene **2g**. The methyl group in naphthalene **2h** acts as a stronger directing group for the coupling reaction than the methoxy group, with the product **3′ah** with the biaryl linkage at the position *ortho* to the methyl group solely obtained. Interestingly, the naphthalene **2i** bearing the resonance-donating bromo group directed the selectivity towards the 3-position of the 1,4-disubstituted naphthalene. Following a similar trend, the product **3′aj** was exclusively obtained in the case of the silyl-protected substrate **2j**, although the product was desilylated. On the other hand, the naphthalenes **2k** and **2l**, bearing electron-withdrawing OTf and OAc protecting groups, directed the reactivities of the naphthalenes towards the 2-position, which is in clear contrast to the two previous results. The polyalkoxybiaryls obtained, and their oxidized quinones, belong to a class of highly valued synthetic intermediates frequently found as core structures in many natural products.[19] Thus, we demonstrated the elaboration of the biaryl **3aa** towards the benzo[*b*]naphthofuran **4** (Scheme 7, for experimental details see the Supporting Information).



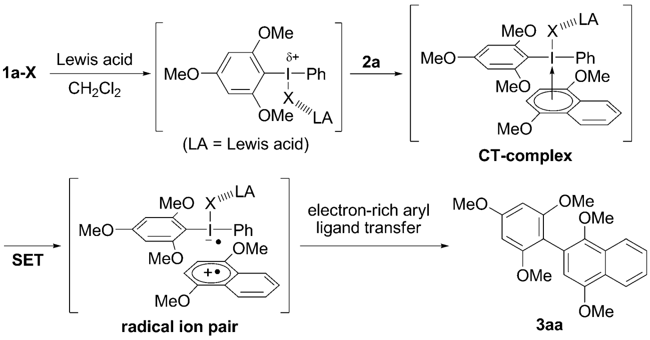
Salt	Naphthalene			Yield of 3 [%] (ratio of regioisomer)[a]
	R4	R5		
1a-OTf	O*i*Bu	H	**2g**	>99 (**3ag**/**3′ag** 50:50)
1a-OTf	Me	H	**2h**	45 (**3′ah** only)
1a-OTf	OMe	Br	**2i**	84 (**3ai**/**3′ai** 17:83)
1a-BF$_4$	OMe	OTBDPS	**2j**	40[b] (**3′aj** only)
1a-BF$_4$	OMe	OTf	**2k**	57 (**3ak**/**3′ak** 70:30)
1a-BF$_4$	OMe	OAc	**2l**	58 (**3al**/**3′al** 71:29)

Scheme 6. Selectivity of the reaction of **1a** with unsymmetrical naphthalenes **2**. Reagents and conditions: iodonium salt **1a-X** (1 equiv), electron-rich naphthalene **2** (1.5 equiv) under the optimized condition. [a] The structure and ratio of the regioisomers **3** and **3′** were determined by ^{1}H NMR and NOE measurements (see the Supporting Information). [b] The desilylated product was obtained.



Scheme 7. Synthesis of benzo[*b*]naphthofuran **4** from biaryl **3aa**.

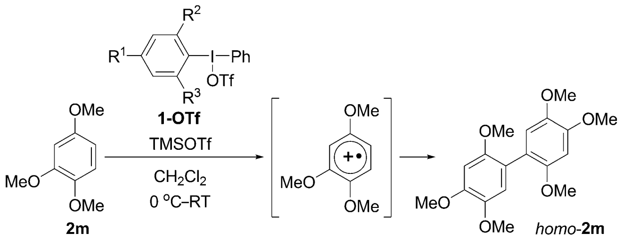
SET oxidation of the diaryliodonium(III) salts 1: With regard to the reaction mechanism, in accord with the results in Table 2 for the SET-sensitive and -inactive substrates **2a–e**, we hypothesize that the SET oxidation process is induced by the polyalkoxybenzene-derived diaryliodonium(III) salts **1** (Scheme 8). The salts **1** are themselves inactive towards



Scheme 8. Mechanistic hypothesis for the SET oxidation leading to the coupling of diaryliodonium salts **1a-X** and aromatic compound **2a**.

the aromatic compounds **2**, and therefore the Lewis acid plays an indispensable role in their activation. It seems that the coordination of the Lewis acid to the ligand X of the salts **1** increases the electrophilicity of the iodine atom, which can then form a charge-transfer (CT) complex with the arene **2**. SET oxidation of the electron-rich arene **2** occurs within the complex to generate the radical-ion pair involving the aromatic radical cation of **2**, to which the electron-rich alkoxyphenyl ring can transfer preferentially over the phenyl group.[20] As experimental support for this radical pathway, we tested the reaction of the salts **1a-X** with arene **2a** in the presence of 1 equiv of a radical scavenger, the galvinoxyl free radical,[21] which resulted in no formation of the coupling product **3aa**.

Further investigation based on this hypothesis provided strong evidence for the SET coupling mechanism. During the coupling of the salt **1a-OTf** with 1,2,4-trimethoxybenzene (**2m**, Scheme 9), the radical homocoupling product *homo*-**2m** was obtained with only a small amount of the coupling product of **1a-OTf** and arene **2m**, which has been attributed to the low oxidation potential ($E^{ox} = 1.12$ V)[16d] and high nucleophilicity[22] of the arene **2m**. Because the formation of the radical cation of the arene **2m** leads to the rapid dimerization and production of the homocoupling product under SET oxidation conditions, we studied the homocoupling reaction of a series of diaryliodonium salts **1**. Similarly to the salt **1a**, the reactive and productive iodonium salts **1c** and **1d** in our coupling reaction (see Scheme 4) initiated the cation-radical-mediated homocoupling of the arene **2m** (yields of 59 and 61%, respectively). In accord with our expectations, the nonproductive salt **1i** having only one methoxy group in our coupling reaction gave only trace amounts of the homocoupling products *homo*-**2m** in the reaction with the arene **2m** due to the poor SET activity towards the generation of the radical cation.



Salt	Yield of *homo*-**2m** [%]
$R^1 = R^2 = R^3$ = OMe **1a**	65[a] (78)[b]
$R^1 = R^2$ = OMe, R^3 = Me **1c**	59[a]
$R^1 = R^2$ = OMe, R^3 = H **1d**	61[a]
R^1 = OMe, $R^2 = R^3$ = H **1i**	trace

Scheme 9. Homocoupling study based on the SET oxidation of the arene **2m**. Reagents and conditions: iodonium salts **1-OTf** (1 equiv), 1,2,4-trimethoxybenzene (**2m**, 2 equiv), TMSOTf (2 equiv), CH_2Cl_2 (0.1 M of **1-OTf**), 0°C–RT. [a] Formation of ca. 10% of the corresponding cross-coupling product **3** was observed (see Scheme 4). [b] **1a-BF$_4$** was used instead of **1a-OTf**.

From these results we can conclude that the diaryliodonium salts **1** based on polyalkoxybenzenes have excellent SET oxidation activities in coupling reactions in comparison with other diaryliodonium salts (Figure 2).

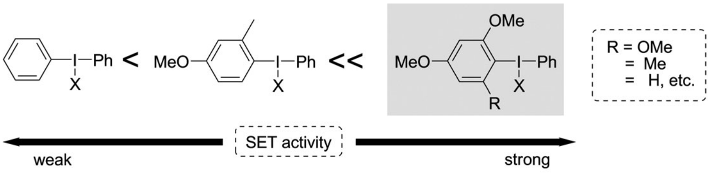
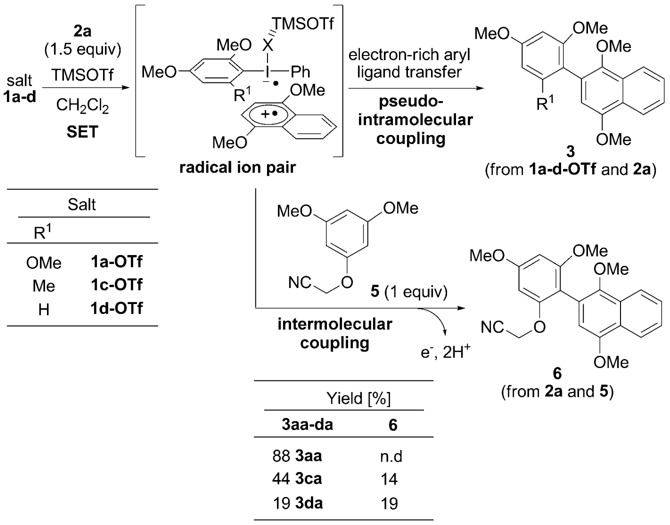


Figure 2. SET oxidation activity of diaryliodonium salts **1**.

Ligand transfer preference in the diaryliodonium(III) salts 1: In our previous studies, the intermediate aromatic radical cations formed by treatment with PIFA reacted with external aromatic nucleophiles to give various biaryls.[9e–m] Thus, the reaction with the diaryliodonium(III) salts **1** would proceed not only in the suggested "pseudo-intramolecular" coupling manner through the collapse of the radical-ion pair (see the mechanism in Scheme 8), but might also cause a similar intermolecular coupling if a second aromatic nucleophile is present.[23] To gain insight into the ligand-transfer properties of the arene ligands in the iodonium salts **1**, we further explored the coupling reactions with 1,4-dimethoxynaphthalene (**2a**) and the salts **1** in the presence of a second nucleophile **5** (Scheme 10). First, the 1,3,5-trimethoxybenzene-derived iodonium salt **1a-OTf** gave the coupling product **3aa** as the sole product even in the presence of the additional aromatic molecule **5**, which implies a fast "pseudo-intramolecular" coupling involving the rapid transfer of the aryl ligand transfer from the salt **1a-OTf**. However, the iodonium salts **1c** and **1d** bearing dimethoxybenzene moieties competitively form the intermolecular coupling product **6** with 1,4-dimethoxynaphthalene (**2a**) and the second arene **5**, probably because of the poorer nucleophilicity of the aryl ligands. The contamination with the latter biaryl **6** during the coupling reactions can be explained by considering the same intermediate as in the reactions leading to the coupling products **3**, which suggests inferior ligand-transfer ability of the radical-ion pair formed from the salts **1c-OTf** and **1d-OTf** with naphthalene **2a** (Scheme 10).



Salt	
R^1	
OMe	**1a-OTf**
Me	**1c-OTf**
H	**1d-OTf**

Yield [%]	
3aa-da	**6**
88 **3aa**	n.d
44 **3ca**	14
19 **3da**	19

Scheme 10. Coupling reaction in the presence of a second aromatic nucleophile **5**. Reagents and conditions: iodonium salts **1-OTf** (1 equiv), **2a** (1.5 equiv), and 1-cyanomethoxy-3,5-dimethoxybenzene **5** (1 equiv), TMSOTf (2 equiv), CH_2Cl_2, 0 °C–RT for 12 h.

Based on this observation, we can summarize the ligand-transfer preference of the diaryliodonium salts **1** as shown in Figure 3. The reactivities of the aryl ligands seem to be in good agreement with the electronic nature and nucleophilicity of the aryl rings. Electron-rich aromatic rings in the salts **1** are advantageous for developing the C–C coupling step via the radical-ion pair. Thus, the ligands in the salts **1** show the same trend in ligand-transfer ability as the SET oxidation activities. Achieving both factors by the introduction of electron-rich aryl moieties is thus highly important for the success of the coupling reactions.

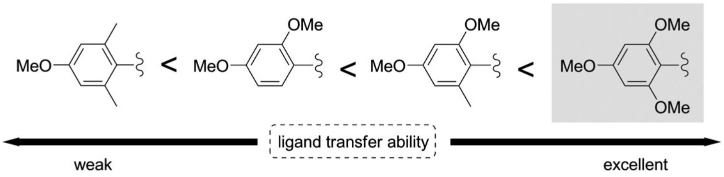


Figure 3. Ligand transfer ability of diaryliodonium salts **1**.

The coupling reactions described in this report show hitherto unknown and unusual chemical behavior of the alkoxybenzene-derived diaryliodonium salts **1** under acidic conditions that lead to SET oxidation reactions and exclusive electron-rich aryl transfer. We have established that electron-rich diaryliodonium salts **1**, especially those having more than two alkoxy groups on the aromatic ring, show excellent performance in SET oxidation reactions and aryl transfer to the generated aromatic radical cations of arenes **2**.

Conclusion

We have succeeded in the oxidative coupling of electron-rich arenes with the polyalkoxybenzene groups of the diaryliodonium(III) salts **1** in an extended study of heteroaromatic iodonium salts.[7] This reaction proceeds without any metal catalyst and thus occurs by a unique mechanism involving single-electron-transfer (SET) oxidation by the diaryliodonium salts **1** followed by electron-rich aryl transfer. Importantly, the presence of the alkoxy groups on the aromatic ring of the salts **1** facilitates the SET oxidation process and aryl transfer. Note that this is the first observation of SET oxidation with diaryliodonium salts, providing a new aspect to the oxidative cross-coupling of polyalkoxybenzene-derived compounds. The diaryliodonium salts, which are usually inert towards many aromatic compounds, are efficiently activated by a Lewis acid thereby enabling the coupling reactions to proceed. In addition, we have revealed that the reactivity of the salts **1** under acidic conditions is quite different to their behavior under known basic conditions. Considering the recent advances in the easy and direct preparation of diaryliodonium salts, including those bearing heteroaromatic ligands,[12] this coupling strategy may contribute to the development of this field as a novel alternative to known coupling technologies and, based on this knowledge, some diverse new C–C coupling products will possibly appear in future studies by exploiting the unique characteristics of the iodonium salts.

Experimental Section

General: Melting points were measured with a Stuart melting point apparatus SMP3 AC input 100 V. ^1H (and ^{13}C NMR) spectra were recorded with a JEOL JMN-400 spectrometer operating at 400 or 300 MHz (100 or 75 MHz) in $CDCl_3$ at 25 °C with tetramethylsilane as an internal standard. The data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), integration, and coupling constant (Hz). The IR spectra were obtained by using an Hitachi 270-50 spectrometer. High-resolution mass spectra (HRMS) were recorded with a JEOL LMS-D 300 spectrometer at the Elemental Analysis Section of Osaka University and Osaka University of Pharmaceutical Sciences.

Diaryliodonium(III) salts **1** were prepared from the corresponding alkoxybenzenes by treatment with [hydroxy(tosyloxy)iodo]benzene (HTIB, 1 equiv) according to our previously reported procedure by using 2,2,2-trifluoroethanol as solvent.[12] The counter ions, X, of the salts **1** were exchanged by treatment with a methanolic aqueous solution of the corresponding metal salts, namely potassium bromide, sodium chloride, sodium tetrafluoroborate, and sodium triflate.[11f] All other chemicals were obtained from commercial suppliers and used as received. Column chromatography for the isolation of the products was carried out on Merck silica gel 60 (230–400 mesh) eluting with hexane and ethyl acetate. Analytical TLC was performed on Merck silica gel, grade 60 F_{254}. The spots and bands were detected by irradiation with UV light (254, 365 nm) and/or by staining with 5% phosphomolybdic acid followed by heating.

General procedure for the oxidative coupling reaction by utilizing diaryliodonium(III) salts 1 with electron-rich arenes 2 (Table 2 and Schemes 4 and 6): Trimethylsilyl triflate (TMSOTf, 0.18 mL, 1.0 mmol) was added to a stirred solution of the diaryliodonium salt **1** (0.50 mmol) and electron-rich arene **2** (0.75 mmol) in dichloromethane (5 mL) under nitrogen atmosphere at 0 °C. The reaction mixture was then stirred overnight as the solution was allowed to warm to ambient temperature. After completion of the reaction (TLC), aqueous saturated sodium hydrogen carbonate was added to the reaction mixture, and the aqueous phase was extracted with dichloromethane three times. The combined extracts were dried over anhydrous sodium sulfate and then evaporated to dryness. The crude residue was purified by column chromatography on silica gel to give the pure coupled biaryls **3**.

*1,4-Dimethoxy-2-(2,4,6-trimethoxyphenyl)naphthalene (**3aa**).* A colorless solid; m.p. 143–145 °C; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=3.62$ (s, 3H), 3.74 (s, 3H), 3.90 (s, 6H), 3.96 (s, 3H), 6.30 (s, 2H), 6.61 (s, 1H), 7.45–7.54 (m, 2H), 8.14 (dd, $J=7.6$, 0.7 Hz, 1H), 8.26 ppm (dd, $J=7.6$, 0.7 Hz, 1H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta=55.3$, 55.5, 55.9, 61.2, 90.8, 108.0, 109.5, 122.1, 122.2, 122.6, 125.0, 126.0, 126.1, 128.7, 147.9, 150.9, 158.7, 160.9 ppm; IR (KBr): $\tilde{\nu}=2937$, 2837, 1606, 1504, 1454, 1415, 1365, 1334, 1222, 1203, 1157, 1126, 1101, 1070, 1037, 999, 970, 948, 844, 812, 771, 567 cm^{-1}; elemental analysis calcd (%) for C$_{21}$H$_{22}$O$_5$: C 71.17, H 6.26; found: C 71.04, H, 6.26.

Competitive coupling reactions of 1,4-dimethoxynaphthalene 2a versus 1-cyanomethoxy-3,5-dimethoxybenzene 5 (Scheme 10): TMSOTf (0.18 mL, 1.00 mmol) was added to a stirred solution containing diaryliodonium salts **1-OTf** (0.50 mmol), 1,4-dimethoxynaphthalene (**2a**; 0.75 mmol), and 1-cyanomethoxy-3,5-dimethoxybenzene (**5**, 0.50 mmol) in dichloromethane (5 mL) under nitrogen atmosphere at 0 °C. The reaction mixture was then stirred at 0 °C to ambient temperature for 12 h. After completion of the reaction (TLC), aqueous saturated sodium hydrogen carbonate was added to the mixture and the aqueous phase was extracted with dichloromethane. The combined extract was dried over anhydrous sodium sulfate and then evaporated to dryness. The crude residue was purified by column chromatography on silica gel to separate the pure cross-coupling biaryls **3aa**, **3cc**,or **3da** and **6**.

*2-(1-Cyanomethoxy-3,5-dimethoxyphenyl)-1,4-dimethoxynaphthalene (**6**).* A colorless amorphous solid; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta=3.57$ (s, 3H), 3.74 (s, 3H), 3.89 (s, 3H), 3.94 (s, 3H), 4.56–4.67 (m, 2H), 6.38–6.40 (m, 2H), 6.56 (s, 1H), 7.47–7.52 (m, 2H), 8.10 (dd, $J=8.0$, 1.0 Hz, 1H), 8.25 ppm (dd, $J=8.0$, 1.0 Hz, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta=54.7$, 55.5, 55.6, 56.0, 61.4, 93.4, 93.8, 107.4, 111.2, 115.4, 121.5, 122.2, 122.3, 125.4, 126.2, 126.3, 128.6, 147.8, 151.2, 155.6, 159.1, 161.0 ppm; IR (KBr): $\tilde{\nu}=3071$, 3004, 2938, 2842, 2251, 1611, 1582, 1505, 1459, 1419, 1390, 1368, 1327, 1269, 1224, 1200, 1160, 1124, 1071, 1047, 998, 971, 948, 912, 814, 771, 738, 670, 651 cm^{-1}; HRMS (EI) calcd for C$_{20}$H$_{21}$NO$_5$ [M]$^+$: 379.1420; found: 379.1414.

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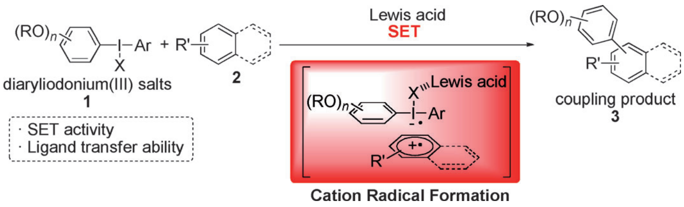

Coupling in the pair: Metal-free oxidative C–C coupling to yield electron-rich biaryls have been achieved by using polyalkoxybenzene-derived diaryliodonium(III) salts as both the oxidant and aryl source. These salts can induce single-electron-transfer (SET) oxidation towards electron-rich aromatic compounds and subsequently transfer the polyalkoxyphenyl group into in situ generated aromatic radical cations to produce biaryl products (see scheme).

Biaryl Coupling

*N. Yamaoka, K. Sumida, I. Itani, H. Kubo, Y. Ohnishi, S. Sekiguchi, T. Dohi, Y. Kita** .... ▮▮▮▮–▮▮▮▮

Single-Electron-Transfer (SET)-Induced Oxidative Biaryl Coupling by Polyalkoxybenzene-Derived Diaryliodonium(III) Salts