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COMMUNICATION

Synthesis of Biaryls via Hypervalent Iodine-Tethered Sigmatropic Rearrangement

Mitsuki Hori,[a] Jing-Dong Guo,[b] Tomoyuki Yanagi,[a] Keisuke Nogi,[a] Takahiro Sasamori,[c] and Hideki Yorimitsu*[a]

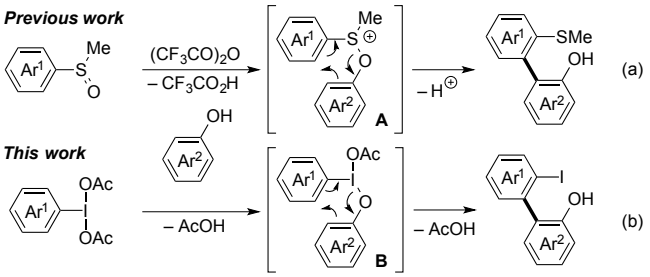
Dedication

Abstract: Metal-free dehydrogenative coupling of aryliodanes with phenols to afford 2-hydroxy-2'-iodobiaryls has been developed. This reaction proceeds via ligand exchange on the hypervalent iodine atom, followed by [3,3] sigmatropic rearrangement, to realize exclusive regioselectivity. This coupling, in combination with *in situ* oxidation by *m*CPBA, facilitates the convenient conversion of iodoarenes into the desired biaryls. The obtained biaryls have convertible iodo and hydroxy groups in close proximity, and are thus synthetically useful, as exemplified by the controlled syntheses of π-expanded furans and a substituted [5] helicene. DFT calculations clearly revealed that the rearrangement is sigmatropic and involves C–C bond formation and I–O bond cleavage in a concerted manner. Acetic acid, which was found to be the best solvent for this protocol, would make the iodine atom more cationic and thus accelerate the sigmatropic rearrangement.

Biaryls are privileged structures in various areas of organic chemistry and in industrial applications. Among numerous methods for the synthesis of biaryls,[1] transition-metal-catalyzed cross-coupling of aryl halides with organometallic reagents is the most reliable. In the last decade, catalytic dehydrogenative C–H/C–H coupling of two aromatic compounds emerged as another promising strategy from the viewpoints of atom and step economy and extensively studied.[2] However, in this method, high catalyst loadings are often required to achieve high efficiency. In addition, contaminations of products by heavy metals would be a fatal problem in research on bioactive agents as well as organic electronic devices.[3] Transition-metal-free dehydrogenative C–H/C–H cross-coupling has been actively investigated as an ideal strategy to overcome these drawbacks.[4]

Recently we developed metal-free C–H/C–H cross-coupling of aryl sulfoxides with phenols in the presence of trifluoroacetic anhydride (Scheme 1a).[5,6] The key intermediate of this reaction is transiently S–O-linked sulfonium **A**, generated through Pummerer-type activation. Sulfonium **A** would undergo charge-accelerated [3,3] sigmatropic rearrangement[7] to eventually afford 2,2'-difunctionalized biaryls in a regioselective fashion. Although this would be an attractive method for the metal-free synthesis of biaryls,[8] the synthetic utility of the resulting sulfanyl-substituted biaryls is limited because transformations of C(sp^2)–S bonds are less explored[9] as compared to those of carbon–halogen bonds.

A direct solution to the aforementioned problem can be the use of aryliodanes, instead of aryl sulfoxides, for the synthesis of more versatile 2'-iodo-2-hydroxybiaryls via intermediate **B** (Scheme 1b). Hypervalent iodine compounds including aryliodanes have been employed as useful and environmentally friendly oxidizing reagents, while reduced iodoarene moieties are generated as "byproducts".[10] Although various transformations such as arylation[11] and alkynylation[12] of nucleophiles with hypervalent iodine reagents have been reported, these reactions proceed at the C–I bonds of the iodine reagents; thus, the iodo moiety is not incorporated into the products. On the other hand, some encouraging precedents involving iodonio-sigmatropic rearrangement have been developed.[13,14] In 1988, Oh found that the reactions of aryliodanes with allylsilanes gave the corresponding *ortho*-allyl iodoarenes via allylaryliodanes.[13a] Later, in an analogous fashion, Ochiai developed *ortho*- propargylation of aryliodanes with propargylsilanes.[13b,c] β-Dicarbonyl compounds also underwent iodonio-sigmatropic rearrangement with aryliodanes to afford the α-arylated products via aryl(vinyloxy)iodanes.[14]



Scheme 1. Dehydrogenative biaryl synthesis tethered by heteroatom in high oxidation state

As a model reaction to confirm our hypothesis, we selected dehydrogenative coupling of 2-naphthol (**1a**) with 2-(diacetoxyiodo)naphthalene (**2a**). In our first trial, simple mixing of **1a** with **2a** in CH_2Cl_2 provided the desired coupling product **3aa** in 38% NMR yield, along with many unidentified byproducts (Table S1, entry 2). After extensive screening of solvents, acetic acid (AcOH) was found to be optimal , and **3aa** was obtained in 70% NMR yield (Table S1, entry 10). It is worth noting that the reaction in the presence of TEMPO or in the dark had a negligible effect on the reaction efficiency (Table S1, entries 11 and 12), which

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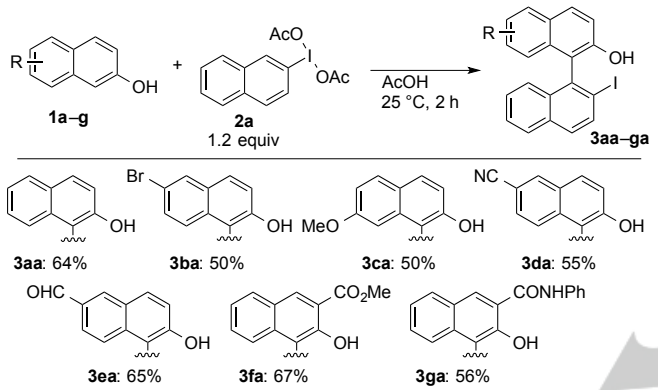
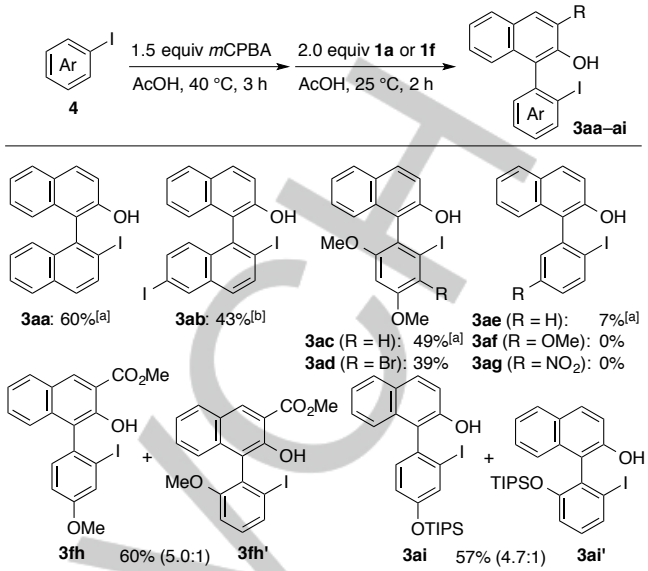
eliminated the possibility of intermediacy of radical species via single-electron oxidation.[4,15]

Under the optimal reaction conditions, **3aa** was isolated in 64% yield (Scheme 2). 6-Bromo-2-hydroxynaphthalene (**1b**) reacted smoothly to yield **3ba**. The reaction of 2-hydroxy-7-methoxynaphthalene (**1c**) furnished the corresponding binaphthyl **3ca** in moderate yield. However, its 6-methoxy isomer afforded a complicated mixture probably because cooperative electron donation from the 6-methoxy and 2-hydroxy groups through conjugation prioritized undesired oxidation of the more electron-rich naphthalene core.[16] Electron-withdrawing groups such as formyl and cyano groups were tolerated under the optimized conditions and binaphthyls **3da**–**ga** were obtained in moderate to good yields.

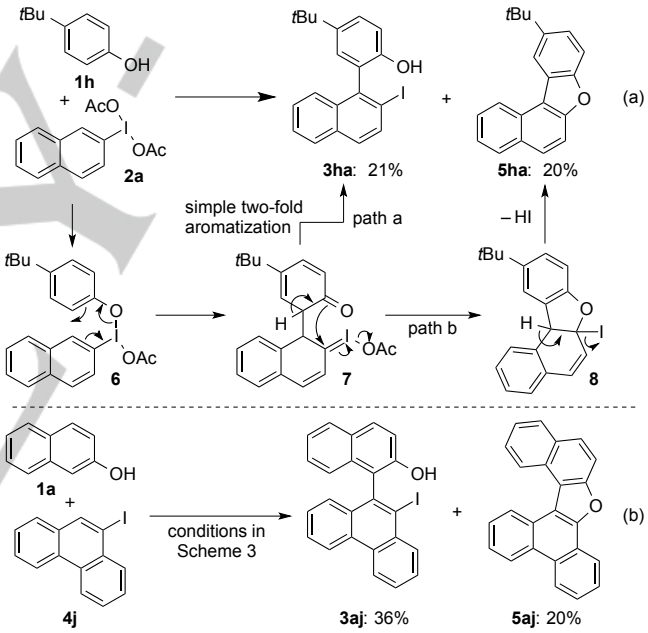


Scheme 2. Scope of naphthols.

We then attempted to explore the scope of aryliodanes. However, preparation of aryliodanes was often troublesome because of their instability and difficulty in purification. We thus attempted to develop a protocol involving oxidation of iodoarenes and subsequent dehydrogenative coupling of naphthols with the aryliodanes generated *in situ*. Gratifyingly, oxidation of 2-iodonaphthalene (**4a**) with dry *m*-chloroperbenzoic acid (*m*CPBA), followed by treatment of 2-naphthol (**1a**), afforded **3aa** in 60% overall yield (Scheme 3). Using this convenient procedure, we could investigate the scope of iodoarenes **4**. Even when a larger amount of *m*CPBA was used, 2,6-diiodonaphthalene (**4b**) underwent selective monoarylation to yield binaphthyl **3ab** as the sole product.[17] The reaction was not limited to iodonaphthalene derivatives; 3,5-dimethoxyiodobenzene (**4c**) and 2-bromo-3,5-dimethoxyiodobenzene (**4d**) also underwent the dehydrogenative coupling to afford **3ac**[18] and **3ad**, respectively. On the other hand, the reaction with iodobenzene (**4e**) gave the product **3ae** in only 7% yield. When 4-methoxyiodobenzene (**4f**) was employed, the desired product **3af** was not obtained. In this case, *ipso* substitution at the C–I bond of **4f** with 2-naphthol (**1a**) proceeded, resulting in C–C bond formation with loss of the iodo moiety to afford 1-(4-methoxyphenyl)-2-naphthol in 59% yield.[19] The electron-deficient 4-nitroiodobenzene (**4g**) did not undergo this reaction and was almost completely recovered. 3-Iodoanisole (**4h**) reacted with naphthol **1f** regioselectively to provide a mixture of **3fh** and **3fh'** in favor of less crowded **3fh**. Good selectivity was observed in the reaction of triisopropylsilyloxy-substituted **1i**.



Scheme 3. Scope of iodoarenes. [a] NMR yield. [b] 2 equiv of *m*CPBA.



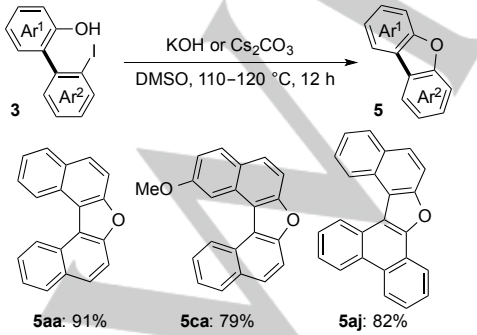
Scheme 4. Cases where two aromatization processes compete.

Not only naphthols (as shown in Scheme 2) but also phenol derivatives participated in the C–C bond forming process.[20] When 4-*tert*-butylphenol (**1h**) was reacted with **2a**, a mixture of the expected biaryl **3ha** and benzonaphthofuran **5ha** was obtained (Scheme 4a).[21] The formation of the mixture provides important information, that is, difference in the rates of rearomatization into a phenolic ring and an iodonaphthalene ring. After the [3,3] sigmatropic rearrangement of intermediate **6**, doubly dearomatized intermediate **7** can go through one of the two pathways: simple double rearomatization to afford biaryl **3ha** (path a) or preferential rearomatization into the more aromatic benzene ring over that into the less aromatic naphthalene, inducing intramolecular nucleophilic attack to yield **8** (path b). Subsequent elimination of HI would furnish benzonaphthofuran **5ha**. A similar trend was observed in the reaction of 9-iodophenanthrene (**4j**) with **1a**, wherein aromatizations into the

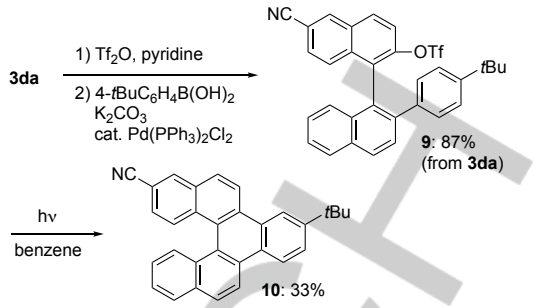
more aromatic naphthalene and less aromatic phenanthrene competed (Scheme 4b). These observations are supportive of our proposed mechanistic scheme involving iodonio-sigmatropic rearrangement.

We carried out DFT calculations to investigate the reaction mechanism further. The coupling of **1a** with **2a** was chosen as a computational model reaction (Figure 1). As expected in Scheme 1, we could find a reaction pathway involving the formation of a transient I–O bond and subsequent [3,3] sigmatropic rearrangement. As the first step, the ligand exchange on the iodine atom was calculated to occur from complex **INT1** with concomitant intramolecular deprotonation of the naphthol by the leaving acetoxy group (**TS1**). The calculated activation barrier to the ligand exchange is 13.3 kcal/mol, reflecting smooth deprotonation via a six-membered cyclic transition state. The subsequent rearrangement from **INT2** to **INT3**[22] was calculated to be sigmatropic: C1–C2 bond formation and I–O5 bond cleavage occur in a concerted manner via **TS2**. The rearrangement computationally proceeds over a rather high activation barrier of 20.4 kcal/mol. Considering that the reaction proceeded very smoothly at room temperature, we conducted calculations for the rearrangement by adding another explicit molecule of acetic acid (**AcOH**) to simulate solvation by hydrogen bonding. Notably, the activation energy for the sigmatropic rearrangement from **AcOH**-coordinating **INT2'** via **AcOH**-coordinating **TS2'** was calculated to be significantly lower (10.5 kcal/mol).[23] At the transition state **TS2'**, the acetoxy ligand on the iodine interacts with the proton of the externally added **AcOH** to render the iodine center more electron-deficient. As Maulide[7] and Shafir[14c,d,24] proposed that a cationic charge at the heteroatom center would accelerate sigmatropic rearrangement, we presume that acetic acid would solvate the acetato ligand on iodine to accelerate the sigmatropic rearrangement.

The synthetic utility of 2-hydroxy-2'-iodobiaryls **3** was next verified. Owing to the high reactivity of their C–I bonds, biaryls **3** underwent intramolecular S_NAr cyclization under basic conditions to afford dinaphthofurans **5aa**, **5ca**, and **5ai** in excellent yields (Scheme 5). As another derivatization, we attempted the controlled synthesis of a [5] helicene derivative with a specific substitution pattern by taking advantage of the different reactivities of the C–I and C–O bonds (Scheme 6). Triflation of **3da** and subsequent iodo-selective Suzuki-Miyaura coupling afforded **9** in 87% yield. Photo-induced ring closure[25] of **9** furnished dorsally benzo-fused [5] helicene **10**.



Scheme 5. Application to the synthesis of π-expanded furans.



Scheme 6. Application to the synthesis of dorsally benzo-fused [5] helicene.

Acknowledgements

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Keywords: biaryl • hypervalent iodine compound • sigmatropic rearrangement • aromaticity • DFT calculations

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[17] The reaction was sluggish, and 45% of **4b** was recovered after treatment of the reaction mixture with $Na_2S_2O_3$. In this case, undesired oxidation of **1a** did not occur and most of **1a** was recovered.

[18] Due to difficulty in separation from byproducts, biaryl **3ac** was isolated as the corresponding benzonaphthofuran after intramolecular S_NAr cyclization (See Supporting Information for details).

[19] *ipso* Substitution of aryliodonium with electron-rich arenes was reported by Kita, see: T. Dohi, M. Ito, N. Yamaoka, K. Morimoto, H. Fujioka, Y. Kita, *Angew. Chem. Int. Ed.* **2010**, *49*, 3334–3337; *Angew. Chem.* **2010**, *122*, 3406–3409.

[20] Although the reactions of **2a** with 4-methoxy- and 4-nitrophenol were conducted, the desired products were not observed. The former gave a complex mixture, and the latter was fully recovered after the reaction. The dehydrogenative coupling of (diacetoxyiodo)benzene with phenol also did not furnish desired 2-hydroxy-2'-iodobiphenyl.

[21] Isolated biaryl **3ha** was not converted into **5ha** in AcOH, the mechanism in Scheme 4 being thus supported.

[22] We depict **INT3** and **INT3'** with explicit C=I double bonds based on careful computational analyses (See the relevant section and Figures S2–S4 in Supporting Information for details).

[23] An extremely high activation barrier (37.9 kcal/mol) was calculated for the possible C–C bond formation between the 3-position of **1a** and the 1-position of **2a** (See Supporting Information for details).

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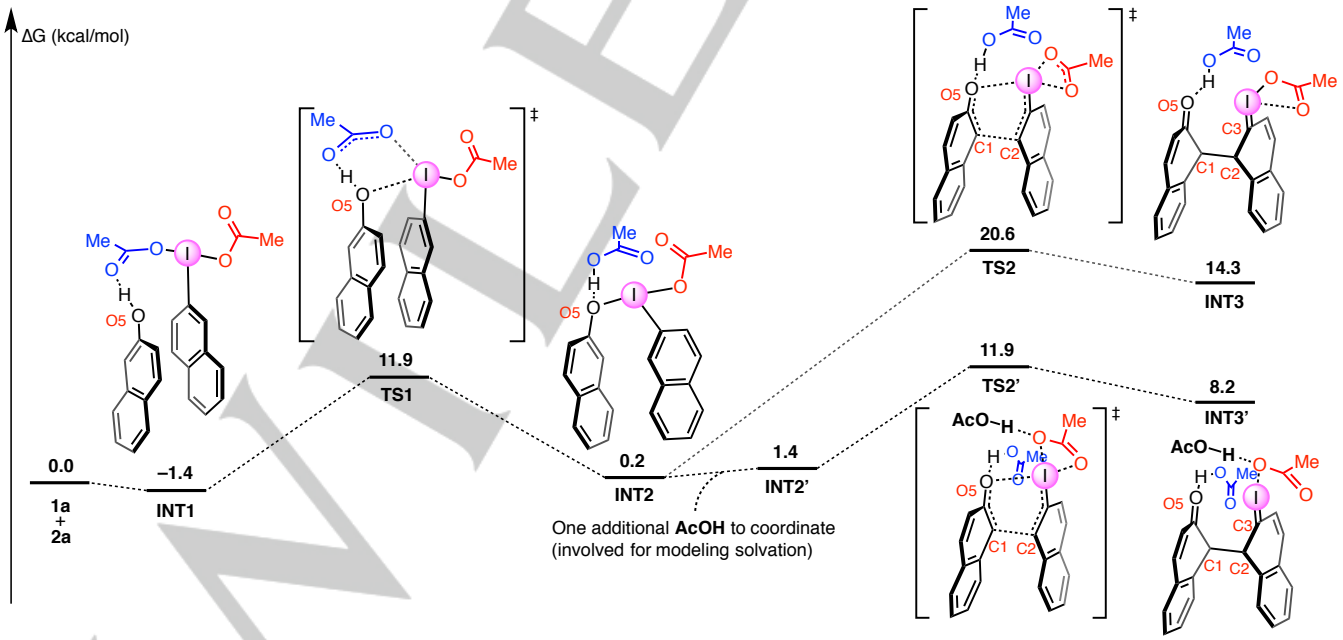

Figure 1. DFT reaction profile calculated at the level of B3LYP-D3(BJ)/Def2-TZVP (for I)/6-311+G(d,p) (for C, H, O) with PCM (AcOH). One innocent **AcOH** that should be included in the pathway from **1a**+**2a** to **INT3** to balance the total energies with those in the pathway including solvation is omitted for clarity.

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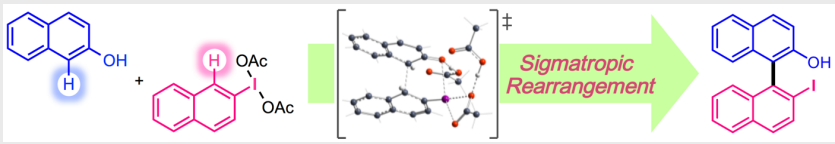

Dehydrogenative coupling of aryliodanes with phenols affords 2-hydroxy-2'-iodobiaryls of synthetic utility, proceeding via ligand exchange on the hypervalent iodine atom followed by [3,3] sigmatropic rearrangement. This coupling, in combination with *in situ* oxidation by *m*CPBA, facilitates the convenient conversion of iodoarenes into the desired biaryls. DFT calculations clearly justify the reaction mechanism and reveals acetic acid solvent would accelerate the sigmatropic rearrangement by hydrogen bonding.

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