Heterocycle Synthesis Hot Paper

DOI: 10.1002/anie.201402925

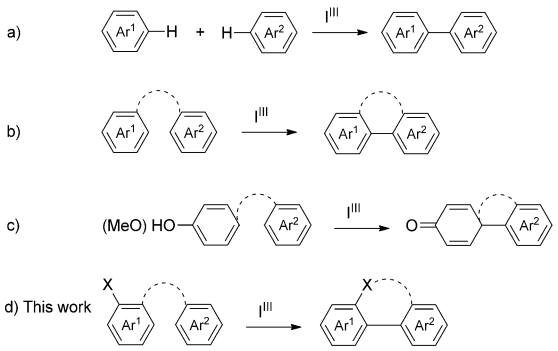
Intramolecular Metal-Free Oxidative Aryl–Aryl Coupling: An Unusual Hypervalent-Iodine-Mediated Rearrangement of 2-Substituted *N*-Phenylbenzamides**

Siyun Shang, Daisy Zhang-Negrerie, Yunfei Du, and Kang Zhao**

Abstract: *Hypervalent-iodine-mediated oxidative coupling of the two aryl groups in either 2-acylamino-N-phenyl-benzamides or 2-hydroxy-N-phenylbenzamides, with concomitant insertion of the ortho-substituted N or O atom into the tether, has been described for the first time. This unusual metal-free rearrangement reaction involves an oxidative C(sp^2)–C(sp^2) aryl–aryl bond formation, cleavage of a C(sp^2)–C(O) bond, and a lactamization/lactonization. Furthermore, unsymmetrical diaryl compounds can be easily obtained by removing the tether within the cyclized product.*

Oxidative coupling of two aryl groups[1] has been intensively studied and has become an exceedingly hot research topic in modern organic synthesis. The direct oxidative coupling reaction between two unfunctionalized aromatic substrates, also known as cross-dehydrogenative coupling (CDC),[2] has been gradually recognized as the most attractive and ideal approach because of its simplicity. Unfortunately, most existing methods require the participation of a transition metal as the catalyst.[3] The metal-free parallels are, however, much less reported, but such explorations have begun to receive attention from organic chemists.[4] In view of the cost as well as environmental concerns of heavy metal involvement, the development of alternative metal-free oxidative coupling systems, especially those that can permit special structural types of coupling, are pressingly worthwhile.

Hypervalent iodine reagents, which are efficient and environmentally benign nonmetal oxidants,[5] have been successfully applied to the oxidative coupling reactions between two arene moieties.[4b,6] A careful literature survey showed that the existing iodine(III)-mediated oxidative coupling reactions can be classified into three types: 1) the intermolecular cross-coupling of two arenes (Scheme 1 a),[4b,6] 2) the intramolecular oxidative coupling of two arenes joined by a tether, thereby affording polycyclic compounds (Scheme 1 b),[7] and 3) the spirocyclization of a tethered phenol derivative involving an *ipso* attack from the side-chain arene during the completion of the oxidative carbon–carbon bond formation (Scheme 1 c).[8] It is worth noting that the phenol ring was converted into a cyclic dienone in the process, and also that in the last two strategies, the tether was kept intact throughout the reaction. Herein, we report the discovery of a novel iodine(III)-mediated rearrangement reaction of the 2-acylamino-*N*-phenylbenzamides **1** and 2-hydroxy-*N*-phenylbenzamides **3**, a process which involves an unusual cleavage of a C(sp^2)–C(O) bond and an intramolecular condensation reaction, after an intramolecular oxidative aryl–aryl bond formation. To our knowledge, this is an unprecedented metal-free protocol for the oxidative coupling of two aryl groups with concomitant insertion of an *ortho*-substituted N or O moiety into the tether (Scheme 1 d).



Scheme 1. Aryl–aryl oxidative coupling mediated by hypervalent iodine reagents.

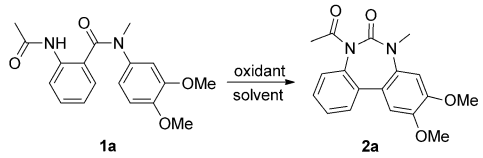
Initially, we were interested in synthesizing dibenzo[*b*,*e*]-[1,4] diazepin-11-one derivatives from **1** through an iodine-(III)-mediated intramolecular aromatic C(sp^2)–N bond formation.[9] But to our surprise, the reaction of 1 equivalent of **1a** with 1.5 equivalents of PIDA in acetonitrile at reflux for 24 hours afforded a 41% yield of the rearranged product **2a** (Table 1, entry 1), the structure of which was unambiguously confirmed by X-ray crystallography.[15] The discovery of this new rearrangement reaction opened the door to a new approach for the construction of the structurally interesting and pharmaceutically[10] important dibenzodihydro-1,3-diazepin-2-one skeletons.[11] The compound **1a** was then used as a model substrate to screen for the optimal reaction conditions. A series of experimental variables, including the amount of the oxidant, the solvent, temperature, additive, and type of hypervalent iodine oxidant were systematically

[*] S. Shang, Dr. D. Zhang-Negrerie, Prof. Dr. Y. Du, Prof. Dr. K. Zhao
Tianjin Key Laboratory for Modern Drug Delivery & High-Efficiency, School of Pharmaceutical Science and Technology
Tianjin University, Tianjin 300072 (China)
and
Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072 (China)
E-mail: duyunfeier@tju.edu.cn
kangzhao@tju.edu.cn

[**] Y.D. acknowledges the National Natural Science Foundation of China (no 21072148) for financial support. We also thank Prof. Richard P. Hsung (University of Wisconsin at Madison) for helpful discussions.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201402925.

Table 1: Optimization of the reaction conditions.[a]



1a 2a

Entry	Oxidant (equiv)	Solvent	*T* [°C]	Yield [%][b]
1	PIDA (1.5)	MeCN	reflux	41
2[c]	PIDA (3.0)	MeCN	reflux	83
3	PIDA (3.0)	DCE	reflux	35
4	PIDA (3.0)	TFE	reflux	23
5	PIDA (3.0)	HFIP	reflux	15
6	PIFA (1.5)	MeCN	RT	n.d.[d]
7	PhIO (1.5)	MeCN	reflux	n.r.
8	IBX (1.5)	MeCN	reflux	n.r.

[a] All reactions were carried out with **1a** (0.5 mmol), PIDA (3.0 equiv), MeCN (10 mL), reflux for 24 h, unless otherwise stated. [b] Yield of isolated product. [c] 14 h. [d] No desired product was detected. DCE = 1,2-dichloroethane, HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol, IBX = *ortho*-iodoxybenzoic acid, n.r. = no reaction, PIDA = phenyliodine-(III) diacetate, TFE = trifluoroethanol, PIFA = phenyliodine(III) bis(trifluoroacetate).

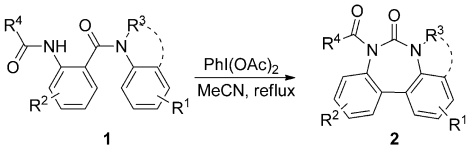
examined (Table 1; see the Supporting Information for details). After several experiments, we found the best conditions to be 3.0 equivalents of PIDA in MeCN at reflux for 14 hours (Table 1, entry 2).[12]

Under the optimal reaction conditions, we examined a wide range of substrates (**1**; Table 2). Results show: 1) The electronic effect of R^1 at the *meta*-position has an effect, that is, electron-donating groups enhance the reaction, with the highest yields obtained from **1a** and **1c**. Moderate electron-withdrawing groups (F or Br) negatively affected the reaction yield (**2g–h**), and strongly electron-withdrawing groups (ester, nitro, or trifluoromethyl) completely impeded the reaction (not shown). The observed R^1 effect concurs with an electrophilic mechanism, wherein the aniline moiety serves as a nucleophile. 2) Steric effects are substantial as high regioselectivity was demonstrated in the formation of a single product from substrates bearing an unsymmetrically substituted aniline moiety, namely, **2a**, **2c**, **2g**, and **2h**. 3) The reaction yield is insensitive to the electronic nature of R^2 (**2i–m**). 4) Other than N-methyl, R^3 can also be an N-isopropyl, N-benzyl, or even N-phenyl group (**2n–p**). 5) The acetyl group (R^4) can be replaced with a *tert*-butoxy or phenyl group (**2q**,**r**). 6) The same method afforded a class of novel tetracyclic heterocyclic compounds (**2s–u**) in moderate yields when starting with N-aryltetrahydroquinoline substrates.

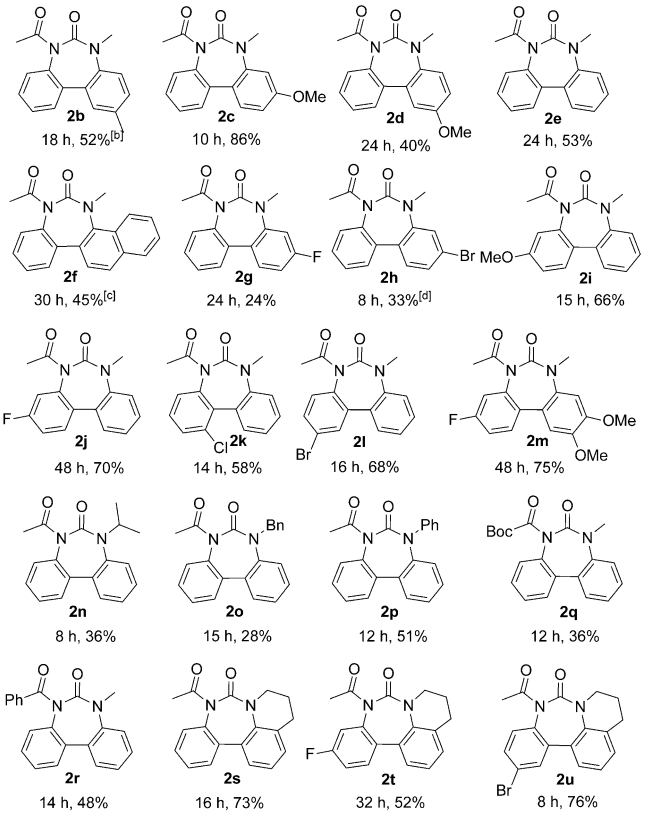
Encouraged by the above findings, we tested out the method on **3a**, where the entire acylamino group in **1e** was replaced by an OH group. Disappointingly, subjecting **3a** to the identical reaction conditions afforded only a complex mixture, with no trace of the expected rearranged product. New studies led us to discover the formation of the spirolactam **4** upon treating **3a** with PIFA (1.5 equiv) in CH_2Cl_2 (0.05 M) at 0 °C for 0.5 hours (Scheme 2; see the Supporting Information for details). To our delight, **4** could be conveniently transformed into the expected dibenzo[*d*,*f*][1,3]oxazepin-6(7*H*)-one (**5a**) after mixing with $BF_3{\cdot}Et_2O$ (0.3 equiv) at room temperature. Considering the fact that both steps could be performed in CH_2Cl_2, a one-pot protocol was envisaged. The most efficient reaction conditions for this reaction were determined to be PIFA (1.3 equiv) in CH_2Cl_2 (0.05 M) at 0 °C for 0.5 hours, followed by introduction of $BF_3{\cdot}Et_2O$ (0.3 equiv) and stirring at room temperature for an additional 0.5 h.[13]

Similarly positive results show that this PIFA/$BF_3{\cdot}OEt_2$ one-pot method can be applied to substrates bearing a variety of R^1 groups (Table 3; **5a–i**), halogens (R^2; **5j**,**k**), and a range of R^3 groups including phenyl, benzyl, and isopropyl (**5l–n**).

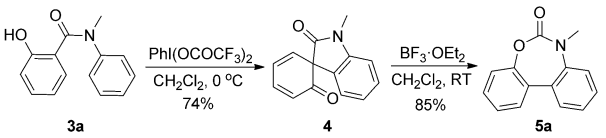
Table 2: Scope of PIDA-mediated dibenzodihydro-1,3-diazepin-2-ones synthesis.[a]



1 2



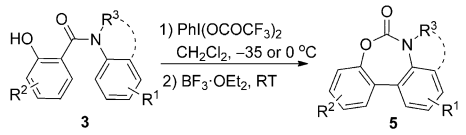
[a] All reactions were carried out with **1** (1 mmol) and PIDA (3.0 equiv) in MeCN (20 mL) at reflux. [b] Yield of isolated product. [c] PIDA (4.0 equiv). [d] PIDA (2.0 equiv).

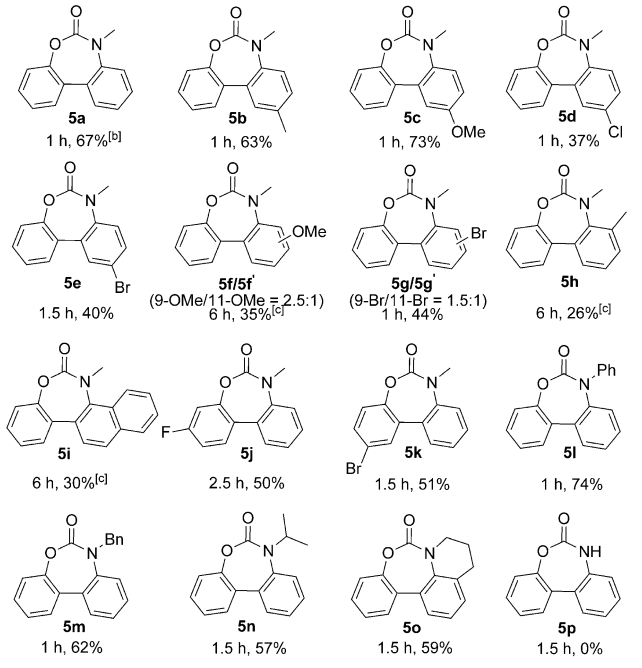


3a 4 5a

Scheme 2. The PIFA/$BF_3{\cdot}Et_2O$-mediated spirocyclization and rearrangement of 2-hydroxy-*N*-methyl-*N*-phenylbenzamide (**3a**).

Table 3: Scope of one-pot synthesis of dibenzo[*d,f*][1,3]oxazepin-6(7*H*)-ones mediated by PIFA/BF_3·Et_2O.[a]

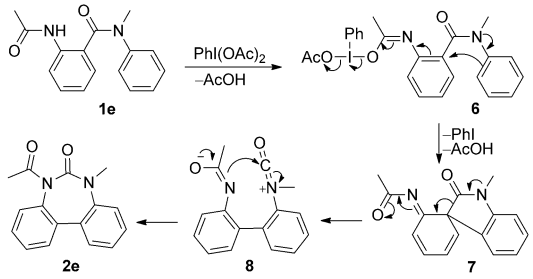




[a] All reactions were carried out with **3** (1 mmol) and PIFA (1.3 equiv) in CH_2Cl_2 (20 mL) at 0 °C for 0.5 h. BF_3·OEt_2 (0.3 equiv) was then added was added at RT. [b] Yield of isolated product. [c] 1.5 equiv of PIFA was added and the reaction mixture stirred at −35 °C for 2.5 h, then BF_3·OEt_2 (0.3 equiv) was added at RT.

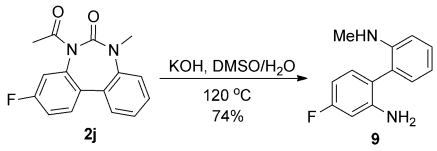
Two regioisomeric products were obtained in the cases of **3f** and **3g** because they contain a substituent at the *meta* position. An unsubstituted amino moiety resulted in none of desired product (**5p**).

A plausible mechanism has been proposed (Scheme 3). Take the reaction of **1e** as an example. The intermediate **6**, initially formed from the reaction of **1e** and PIDA and loss of one molecule of acetic acid, gives rise to the spiro-intermediate **7** after a nucleophilic *ipso* attack of the aniline ring on the electron-deficient aromatic carbon atom of the anthranilic ring in **6**, accompanied by the loss of one molecule of phenyl iodide and acetic acid. The presence of the electron-withdrawing acyl group on the imine N and the lone pair on the amide N then facilitate a rapid ring opening of **7** to give the intermediate **8**. Finally, lactamization of **8** provides the title compound **2e**. Although **7** was not directly observed during the reaction, the isolation of **4** in the two-step reaction of **3a** provides convincing evidence for the reaction sequence proposed.

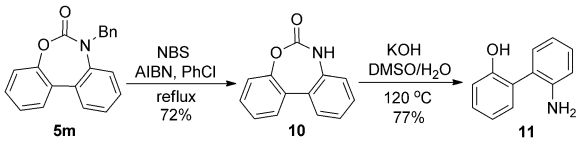


Scheme 3. A plausible mechanistic pathway.

This particular rearrangement reaction was also applied to the synthesis of biaryls. Treating **2j** with KOH (10 equiv) in DMSO/H_2O (v/v, 1:1) at 120 °C for 5 hours provided the diaryl **9** in a satisfactory 74% yield (Scheme 4). Similarly, the biaryl **11** could be formed through the cleavage of the carbamate group in **5m** (Scheme 5). The transformation involved a known debenzylation procedure[14] and subsequent hydrolysis conditions.



Scheme 4. Conversion of **2j** into **9** through base-promoted hydrolysis. DMSO = dimethylsulfoxide.



Scheme 5. Conversion of **5m** into **11** through debenzylation and hydrolysis. AIBN = 2,2′-azobis(2-methylpropionitrile), NBS = *N*-bromosuccinimide.

In conclusion, we have discovered an unprecedented iodine(III)-mediated tandem reaction involving the dehydrogenative coupling of two aryl groups, the cleavage of a C-(sp^2)–C(O) bond, and final intramolecular cyclization. This novel protocol provides easy access to a series of diversely functionalized dibenzodihydro-1,3-diazepin-2-ones (**2**) and dibenzo[*d,f*][1,3]oxazepin-6(7*H*)-ones (**5**), which are not readily accessible by any known approaches. Furthermore, unsymmetrical diaryl compounds can be easily obtained by removing the tether within the cyclized product.

Received: March 2, 2014
Revised: March 31, 2014
Published online: ■■ ■■, ■■■■

Keywords: cross-coupling · heterocycles · hypervalent iodine reagents · rearrangement

[1] Selected reviews for oxidative coupling of two aryl groups: a) A. F. Littke, G. C. Fu, *Angew. Chem. Int. Ed.* **2002**, *41*, 4176;

Angew. Chem. **2002**, *114*, 4350; b) L. Yin, J. Liebscher, *Chem. Rev.* **2007**, *107*, 133; c) A. A. O. Sarhan, C. Bolm, *Chem. Soc. Rev.* **2009**, *38*, 2730; d) C. A. Fleckenstein, H. Plenio, *Chem. Soc. Rev.* **2010**, *39*, 694; e) G. Cahiez, A. Moyeux, *Chem. Rev.* **2010**, *110*, 1435; f) E. Negishi, *Angew. Chem. Int. Ed.* **2011**, *50*, 6738; *Angew. Chem.* **2011**, *123*, 6870; g) G. Bringmann, T. Gulder, T. A. M. Gulder, M. Breuning, *Chem. Rev.* **2011**, *111*, 563; h) C. S. Yeung, V. M. Dong, *Chem. Rev.* **2011**, *111*, 1215; i) N. Kuhl, M. N. Hopkinson, J. Wencel-Delord, F. Glorius, *Angew. Chem. Int. Ed.* **2012**, *51*, 10236; *Angew. Chem.* **2012**, *124*, 10382; j) M. Grzybowski, K. Skonieczny, H. Butenschçn, D. T. Gryko, *Angew. Chem. Int. Ed.* **2013**, *52*, 9900; *Angew. Chem.* **2013**, *125*, 10084.

[2] Selected references for cross-dehydrogenative coupling of two arenes: a) C. He, S. Fan, X. Zhang, *J. Am. Chem. Soc.* **2010**, *132*, 12850; b) P. Xi, F. Yang, S. Qin, D. Zhao, J. Lan, G. Gao, C. Hu, J. You, *J. Am. Chem. Soc.* **2010**, *132*, 1822; c) X. Bugaut, F. Glorius, *Angew. Chem. Int. Ed.* **2011**, *50*, 7479; *Angew. Chem.* **2011**, *123*, 7618; d) M. Nishino, K. Hirano, T. Satoh, M. Miura, *Angew. Chem. Int. Ed.* **2012**, *51*, 6993; *Angew. Chem.* **2012**, *124*, 7099; e) C. He, Q. Min, X. Zhang, *Organometallics* **2012**, *31*, 1335; f) R. Odani, K. Hirano, T. Satoh, M. Miura, *J. Org. Chem.* **2013**, *78*, 11045; g) Y. Shang, X. Jie, H. Zhao, P. Hu, W. Su, *Org. Lett.* **2014**, *16*, 416.

[3] Selected references for metal-catalyzed oxidative couplings: a) K. L. Hull, M. S. Sanford, *J. Am. Chem. Soc.* **2007**, *129*, 11904; b) D. R. Stuart, E. Villemure, K. Fagnou, *J. Am. Chem. Soc.* **2007**, *129*, 12072; c) S. Potavathri, K. C. Pereira, S. I. Gorelsky, A. Pike, A. P. LeBris, B. DeBoef, *J. Am. Chem. Soc.* **2010**, *132*, 14676; d) X. Zhao, C. S. Yeung, V. M. Dong, *J. Am. Chem. Soc.* **2010**, *132*, 5837; e) X. Wang, D. Leow, J. Yu, *J. Am. Chem. Soc.* **2011**, *133*, 13864; f) H. Li, J. Liu, C. Sun, J. Li, Z. Shi, *Org. Lett.* **2011**, *13*, 276; g) A. N. Campbell, E. B. Meyer, S. S. Stahl, *Chem. Commun.* **2011**, *47*, 10257; h) J. Wencel-Delord, C. Nimphius, F. W. Patureau, F. Glorius, *Angew. Chem. Int. Ed.* **2012**, *51*, 2247; *Angew. Chem.* **2012**, *124*, 2290.

[4] Selected references for metal-free oxidative couplings: a) T. Morofuji, A. Shimizu, J. Yoshida, *Angew. Chem. Int. Ed.* **2012**, *51*, 7259; *Angew. Chem.* **2012**, *124*, 7371; b) M. Ito, H. Kubo, I. Itani, K. Morimoto, T. Dohi, Y. Kita, *J. Am. Chem. Soc.* **2013**, *135*, 14078; c) A. Kirste, G. Schnakenburg, F. Stecker, A. Fischer, S. R. Waldvogel, *Angew. Chem. Int. Ed.* **2010**, *49*, 971; *Angew. Chem.* **2010**, *122*, 983; d) A. Kirste, B. Elsler, G. Schnakenburg, S. R. Waldvogel, *J. Am. Chem. Soc.* **2012**, *134*, 3571; e) L. Zhai, R. Shukla, S. H. Wadumethrige, R. Rathore, *J. Org. Chem.* **2010**, *75*, 4748; f) H. Jasch, J. Scheumann, M. R. Heinrich, *J. Org. Chem.* **2012**, *77*, 10699; g) J. Robertson, M. J. Palframan, S. A. Shea, K. Tchabanenko, W. P. Unsworth, C. Winters, *Tetrahedron* **2008**, *64*, 11896.

[5] Selected reviews on hypervalent iodine reagents: a) J. P. Brand, D. F. González, S. Nicolai, J. Waser, *Chem. Commun.* **2011**, *47*, 102; b) V. V. Zhdankin, P. J. Stang, *Chem. Rev.* **2002**, *102*, 2523; c) P. J. Stang, *J. Org. Chem.* **2003**, *68*, 2997; d) T. Wirth, *Angew. Chem. Int. Ed.* **2005**, *44*, 3656; *Angew. Chem.* **2005**, *117*, 3722; e) R. M. Moriarty, *J. Org. Chem.* **2005**, *70*, 2893; f) R. D. Richardson, T. Wirth, *Angew. Chem. Int. Ed.* **2006**, *45*, 4402; *Angew. Chem.* **2006**, *118*, 4510; g) V. V. Zhdankin, P. J. Stang, *Chem. Rev.* **2008**, *108*, 5299; h) T. Dohi, Y. Kita, *Chem. Commun.* **2009**, 2073; i) V. V. Zhdankin, *J. Org. Chem.* **2011**, *76*, 1185; j) Q. Ding, Y. Ye, R. Fan, *Synthesis* **2013**, 1; k) V. V. Zhdankin, *Hypervalent Iodine Chemistry*, Wiley, Chichester, **2014**.

[6] Selected references for hypervalent iodine reagent mediated oxidative coupling reaction between two arene moieties: a) T. Dohi, M. Ito, K. Morimoto, M. Iwata, Y. Kita, *Angew. Chem. Int. Ed.* **2008**, *47*, 1301; *Angew. Chem.* **2008**, *120*, 1321; b) Y. Kita, K. Morimoto, M. Ito, C. Ogawa, A. Goto, T. Dohi, *J. Am. Chem. Soc.* **2009**, *131*, 1668; c) K. Morimoto, N. Yamaoka, C. Ogawa, T. Nakae, H. Fujioka, T. Dohi, Y. Kita, *Org. Lett.* **2010**, *12*, 3804; d) T. Dohi, M. Ito, I. Itani, N. Yamaoka, K. Morimoto, H. Fujioka, Y. Kita, *Org. Lett.* **2011**, *13*, 6208; e) K. Morimoto, K. Sakamoto, Y. Onishi, T. Miyamoto, M. Ito, T. Dohi, Y. Kita, *Chem. Eur. J.* **2013**, *19*, 8726; f) R. Samanta, J. Lategahnz, A. P. Antonchick, *Chem. Commun.* **2012**, *48*, 3194; g) S. K. Reddy Parumala, R. K. Peddinti, *Org. Lett.* **2013**, *15*, 3546; h) E. Faggi, R. M. Sebastian, R. Pleixats, A. Vallribera, A. Shafir, A. R. Gimeno, C. R. Arellano, *J. Am. Chem. Soc.* **2010**, *132*, 17980.

[7] Selected references for hypervalent iodine reagent mediated intramolecular oxidative coupling of two arenes: a) Y. Kita, M. Gyoten, M. Ohtsubo, H. Tohma, T. Takada, *Chem. Commun.* **1996**, 1481; b) T. Takada, M. Arisawa, H. Gyoten, R. Hamada, H. Tohma, Y. Kita, *J. Org. Chem.* **1998**, *63*, 7698; c) I. Moreno, I. Tellitu, J. Etayo, R. SanMartin, E. Dominguez, *Tetrahedron* **2001**, *57*, 5403; d) I. Isabel, I. Tellitu, E. Dominguez, R. SanMartin, *Eur. J. Org. Chem.* **2002**, *67*, 2126.

[8] Selected references for hypervalent iodine reagent mediated spirocyclization of a tethered phenol derivative: a) H. Fujioka, H. Komatsu, T. Nakamura, A. Miyoshi, K. Hata, J. Ganesh, K. Murai, Y. Kita, *Chem. Commun.* **2010**, *46*, 4133; b) T. Dohi, N. Takenaga, K. I. Fukushima, T. Uchiyama, D. Kato, M. Shiro, H. Fujioka, Y. Kita, *Chem. Commun.* **2010**, *46*, 7697; c) I. R. Baxendale, S. V. Ley, C. Piutti, *Angew. Chem. Int. Ed.* **2002**, *41*, 2194; *Angew. Chem.* **2002**, *114*, 2298; d) L. Moisan, M. Wagner, S. Comesse, E. Doris, *Tetrahedron Lett.* **2006**, *47*, 9093; e) T. Dohi, Y. Minamitsuji, A. Maruyama, S. Hirose, Y. Kita, *Org. Lett.* **2008**, *10*, 3559.

[9] Selected references for $C(sp^2)$–N bond formation mediated by hypervalent iodine reagents: a) R. Samanta, J. O. Bauer, C. Strohmann, A. P. Antonchick, *Org. Lett.* **2012**, *14*, 5518; b) Y. Amano, K. Inoue, S. Nishiyama, *Synlett* **2008**, 134; c) D. Kajiyama, K. Inoue, Y. Ishikawa, S. Nishiyama, *Tetrahedron* **2010**, *66*, 9779; d) A. P. Antonchick, R. Samanta, K. Kulikov, J. Lategahn, *Angew. Chem. Int. Ed.* **2011**, *50*, 8605; *Angew. Chem.* **2011**, *123*, 8764; e) S. H. Cho, J. Yoon, S. Chang, *J. Am. Chem. Soc.* **2011**, *133*, 5996; f) J. Huang, Y. He, Y. Wang, Q. Zhu, *Chem. Eur. J.* **2012**, *18*, 13964; g) S. K. Alla, R. K. Kumar, P. Sadhu, T. Punniyamurthy, *Org. Lett.* **2013**, *15*, 1334; h) R. Samanta, K. Matcha, A. P. Antonchick, *Eur. J. Org. Chem.* **2013**, 5769.

[10] W. E. Kreighbaum, H. C. Scarborough, *J. Med. Chem.* **1964**, *7*, 310.

[11] Selected references for construction of the dibenzodihydro-1,3-diazepin-2-one skeleton: a) A. I. Roshchin, R. G. Kostyanovsky, *Mendeleev Commun.* **2003**, *13*, 275; b) A. K. Ganguly, C. H. Wang, D. Biswas, J. Misiaszek, A. Micula, *Tetrahedron Lett.* **2006**, *47*, 5539; c) S. Kumar, R. Pratap, A. Kumar, B. Kumar, V. K. Tandon, V. J. Ram, *Tetrahedron* **2013**, *69*, 4857.

[12] For previous examples of using excessive amounts of PIDA (3–5 equiv) with heating (60–140 °C), see: a) H. Togo, Y. Hoshina, T. Muraki, H. Nakayama, M. Yokoyama, *J. Org. Chem.* **1998**, *63*, 5193; b) H. J. Kim, J. Kim, S. H. Cho, S. Chang, *J. Am. Chem. Soc.* **2011**, *133*, 16382; c) A. A. Kantak, S. Potavathri, R. A. Barham, K. M. Romano, B. DeBoef, *J. Am. Chem. Soc.* **2011**, *133*, 19960.

[13] We also performed the reaction by using a combination of 20 % mol PhI and 3.0 equiv of *m*CPBA as the terminal oxidant. However, only a 30 % yield of **5a** was obtained (see the Supporting Information for details).

[14] S. R. Baker, A. F. Parsons, M. Wilson, *Tetrahedron Lett.* **1998**, *39*, 331.

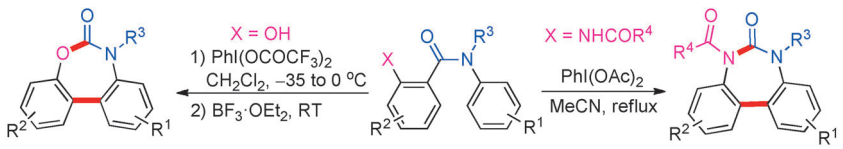
[15] http:///CCDC 973387 (**2a**), formula: $C_{18}H_{18}N_2O_4$, unit cell parameters: $a = 8.6936(17)$, $b = 9.901(2)$, $c = 10.245(2)$ Å, P-1.

Communications

Heterocycle Synthesis

S. Shang, D. Zhang-Negrerie, Y. Du,*
K. Zhao* ——————— ■■■■–■■■■

Intramolecular Metal-Free Oxidative Aryl–Aryl Coupling: An Unusual Hypervalent-Iodine-Mediated Rearrangement of 2-Substituted *N*-Phenylbenzamides



Making (re)arrangements: Hypervalent-iodine-mediated oxidative coupling of the two aryl groups in either 2-acylamino-*N*-phenyl-benzamides or 2-hydroxy-*N*-phenylbenzamides with concomitant insertion of the *ortho*-substituted N or O atom into the tether is described. This unusual metal-free rearrangement reaction involves an oxidative C(sp^2)–C(sp^2) aryl–aryl bond formation, cleavage of a C(sp^2)–C(O) bond, and a lactamization/lactonization.