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Iodo-Carbocyclization of Electron-Deficient Alkenes: Synthesis of Oxindoles and Spirooxindoles

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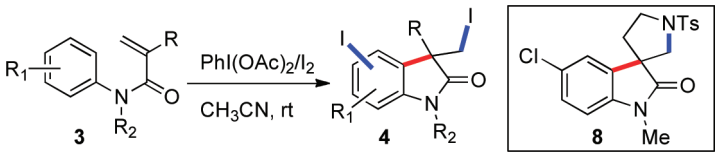
ABSTRACT



Cyclisative carbo-iodination of *N*-alkyl-*N*-arylacrylamide derivatives (3) in the presence of PhI(OAc)$_2$/I$_2$ afforded functionalized 3-(iodomethyl)-3-substituted-indolin-2-ones (4) in good to excellent yields. With a suitably functionalized linear amide, spirooxindole 8 was prepared in a one-pot fashion *via* a sequence of iodo-arylation followed by an *in situ* base-promoted intramolecular S$_N$2 reaction.

Halonium-induced cyclizations of heteroatom-tethered olefins have emerged as powerful methods for the construction of heterocycles.[1] On the other hand, halocarbocyclization of polyenes is far less developed,[2] although such processes are known in the biogenesis of halogenated natural products.[3] Notable recent achievements in this field are as follows: (a) Ishiraha's enantioselective cyclization of 1,5-dienes in the presence of chiral phosphoramidite-complexed *N*-iodosuccinimide (NIS);[4] (b) Barluenga's bis(pyridine)iodonium tetrafluoroborate (Py$_2$IBF$_4$)/HBF$_4$-promoted iodoarylation of *N*-protected-*N*-allylanilines (**1**) to afford 1,2,3,4-tetrahydroquinolines (**2**, Scheme 1, eq 1);[5] and (c) Snyder's BDSB (bromodiethylsulfonium bromopentachloroantimonate) promoted cyclization of polyenes.[6] In all of these examples, electron-rich olefins are used as cyclization partners, and in the case of 1,5-dienes, formal 6-*endo*-trig cyclization is strongly favored over the alternative 5-*exo*-trig mode[7] in accord with the Eschenmoser–Stork postulate (Scheme 1, eq 1).[8] We report herein that a combination of two reagents, PhI(OAc)$_2$ and I$_2$, is capable of promoting the iodoarylation of α-substituted

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(1) Reviews: (a) Togo, H.; Iida, S. *Synlett* **2006**, 2159–2175. (b) Mphahlele, M. J. *Molecules* **2009**, *14*, 4814–4837. (c) Chen, G.; Ma, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 8306–8308. For a recent enantioselective oxylactonization, see: (d) Fujita, M.; Yoshida, Y.; Miyata, K.; Wakisaka, A.; Sugimura, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 7068–7071.

(2) For earlier examples of bromocarbocyclization, see: (a) van Tamelen, E. E.; Hessler, E. J. *J. Chem. Soc., Chem. Commun.* **1966**, 411–413. (b) González, A. G.; Martín, J. D.; Pérez, C.; Ramírez, M. A. *Tetrahedron Lett.* **1976**, *17*, 137–138. (c) Kato, T.; Ichnose, I.; Kamoshida, A.; Kitahara, Y. *J. Chem. Soc., Chem. Commun.* **1976**, 518–519. Very low yields were obtained in these earlier examples. For an example of iodocarbocyclization, see: (d) Barluenga, J.; González, J. M.; Campos, P. J.; Asensio, G. *Angew. Chem., Int. Ed.* **1988**, *27*, 1546–1547.

(3) Butler, A.; Carter-Franklin, J. N. *Nat. Prod. Rep.* **2004**, *21*, 180–188.

(4) Sakakura, A.; Ukai, A.; Ishihara, K. *Nature* **2007**, *445*, 900–903.

(5) Barluenga, J.; Trincado, M.; Rubio, E.; Gonzales, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 3416–3417.

(6) (a) Snyder, S. A.; Treitler, D. S. *Angew. Chem., Int. Ed.* **2009**, *48*, 7899–7903. (b) Snyder, S. A.; Treitler, D. S.; Brucks, A. P. *J. Am. Chem. Soc.* **2010**, *132*, 14303–14314.

(7) Note that 5-*exo*-trig cyclization is generally favored over the alternative 6-*endo*-trig cyclization in iodonium-promoted cyclization reactions of heteroatom-tethered alkenes in accord with the Baldwin's rules. However, the reverse is true in the cyclization of 1,5-dienes. For Baldwin's rules, see: Baldwin, J. E. *J. Chem. Soc., Chem. Commun.* **1976**, 734–736.

(8) (a) Stork, G.; Burgstahler, A. W. *J. Am. Chem. Soc.* **1955**, *77*, 5068–5077. (b) Eschenmoser, A.; Ruzicka, L.; Jeger, O.; Arigoni, D. *Helv. Chim. Acta* **1955**, *38*, 1890–1904. For a recent perspective on this subject, see: (c) Eschenmoser, A.; Arigoni, D. *Helv. Chim. Acta* **2005**, *88*, 3011–3050.

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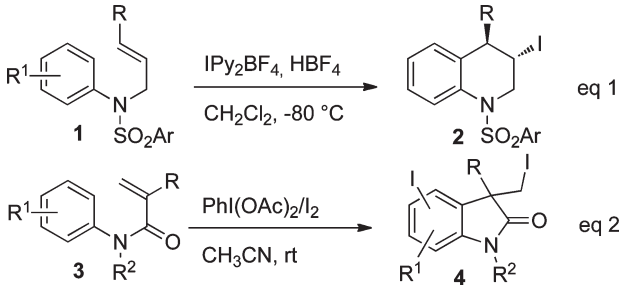
N-arylacrylamide derivatives (**3**) to afford 3,3′-disubstituted oxindoles (**4**, Scheme 1, eq 2). To the best of our knowledge, this work constitutes the first examples of iodo-carbocyclization of electron-deficient olefins. The unique cyclization mode is also noteworthy as it proceeds *via* an unusual formal 5-*exo*-trig cyclization mode in sharp contrast to the cyclization of structurally similar *N*-protected-*N*-allylanilines (**1**).[9]

Scheme 1. Different Cyclization Modes for Iodoarylation



3,3′-Disubstituted oxindoles are highly valuable synthetic targets due to their presence in a wide range of natural products, pharmaceuticals, and agrochemicals.[10] Among known synthetic strategies, palladium-catalyzed cyclization of *ortho*-functionalized anilides was particularly successful.[11] More recently, metal-catalyzed C−H activation[12]/cyclization processes starting from unfunctionalized anilides have been developed.[13,14] We have been involved in the development of a palladium-catalyzed synthesis of oxindoles[15] and have recently reported an oxidative palladium-catalyzed carbo-heterofunctionalization of alkenes **3** involving a direct aromatic C−H functionalization step.[16] Stimulated by the recent development of halonium-mediated carbocyclization processes,[4−6] we became interested in investigating the cyclization of **3** under metal-free conditions using **3a** as a model substrate.

As shown in Table 1, our initial survey of reaction conditions using molecular iodine (I_2), iodine monochloride (ICl), or Barluenga's reagent (Py_2IBF_4/HBF_4)[17] as iodonium sources showed them to be inefficient at promoting the desired transformation. However, a combination of oxidant [$PhI(OAc)_2$, IBX (2-iodoxybenzoic acid), AgOAc, or $PhI(OCOCF_3)_2$] with iodine in acetic acid (AcOH) furnished in each case the oxindole **4a**, with $PhI(OAc)_2/I_2$ being the most effective.[18] In sharp contrast to the cyclization of **1** reported by Barluenga (eq 1, Scheme 1),[5] a 5-*exo*-trig iodo-carbocyclization occurred in our case leading to oxindole with concurrent iodination of the aromatic ring.

Using $PhI(OAc)_2/I_2$ as an iodonium source, we next investigated the solvent effect. The reaction was less efficient in more acidic media (TFA, entry 8, Table 1) and failed to take place in MeOH (entry 9). Among other screened solvents [CH_2Cl_2, THF, EtOAc, 1,2-dichloroethane (DCE), dioxane, MeCN, DMF, DMSO], acetonitrile (MeCN) was found to be the most efficient one to

(9) For synthesis of indoles via formal 5-*endo*-dig iodo-heterocyclization, see: (a) Barluenga, J.; Trincado, M.; Rubio, E.; Gonzalez, J. M. *Angew. Chem., Int. Ed.* **2003**, *42*, 2406–2409. (b) Amjad, M.; Knight, D. W. *Tetrahedron Lett.* **2004**, *45*, 539–541. (c) Yue, D.; Larock, R. C. *Org. Lett.* **2004**, *6*, 1037–1040. For iodoarylation of electron-rich enamine to 3*H*-indoles via a formal 5-*endo*-trig iodoarylation process, see: (d) He, Z.; Li, H.; Li, Z. *J. Org. Chem.* **2010**, *75*, 4636–4639. (e) For $PhI(OAc)_2$-mediated aminotrifluoroacetoxylation of alkenes, see: Lovick, H. M.; Michael, F. E. *J. Am. Chem. Soc.* **2010**, *132*, 1249–1251.

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(14) For related palladium-catalyzed C−N bond formation: (a) Wasa, M.; Yu, J.-Q. *J. Am. Chem. Soc.* **2008**, *130*, 14058–14059. (b) Miura, T.; Ito, Y.; Murakami, M. *Chem. Lett.* **2009**, *38*, 328–329.

(15) (a) Bonnaterre, F.; Bois-Choussy, M.; Zhu, J. *Org. Lett.* **2006**, *8*, 4351–4354. (b) Pinto, A.; Neuville, L.; Retailleau, P.; Zhu, J. *Org. Lett.* **2006**, *8*, 4927–4930. (c) Pinto, A.; Jia, Y.; Neuville, L.; Zhu, J. *Chem.—Eur. J.* **2007**, *13*, 961–967. (d) Pinto, A.; Neuville, L.; Zhu, J. *Angew. Chem., Int. Ed.* **2007**, *46*, 3291–3295. (e) Jaegli, S.; Vors, J.-P.; Neuville, L.; Zhu, J. *Synlett.* **2009**, 2997–2999. (f) Pinto, A.; Neuville, L.; Zhu, J. *Tetrahedron Lett.* **2009**, *50*, 3602–3605. (g) Erb, W.; Neuville, L.; Zhu, J. *J. Org. Chem.* **2009**, *74*, 3109–3115. (h) Jaegli, S.; Erb, W.; Retailleau, P.; Vors, J.-P.; Neuville, L.; Zhu, J. *Chem.—Eur. J.* **2010**, *16*, 5863–5867.

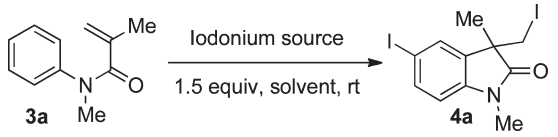
(16) Jaegli, S.; Dufour, J.; Wei, H.-L.; Piou, T.; Duan, X.-H.; Vors, J.-P.; Neuville, L.; Zhu, J. *Org. Lett.* **2010**, *12*, 4498–4501.

(17) Barluenga, J.; Gonzalez, J. M.; Campos, P. J.; Asensio, G. *Angew. Chem., Int. Ed.* **1985**, *24*, 319–320.

(18) (a) Concepcion, J. I.; Francisco, C. G.; Hernández, R.; Salazar, J. A.; Suárez, E. *Tetrahedron Lett.* **1984**, *25*, 1953–1956. (b) Courtneidge, J. L.; Lusztyk, J.; Pagé, D. *Tetrahedron Lett.* **1994**, *35*, 1003–1006. For recent examples using $PhI(OAc)_2/I_2$ in palladium-catalyzed oxidative functionalization, see: (c) Wang, D.-H.; Hao, X.-S.; Wu, D.-F.; Yu, J.-Q. *Org. Lett.* **2006**, *8*, 3387–3390. (d) Mei, T. S.; Giri, R.; Maugel, N.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2008**, *47*, 5215–5219. (e) Li, J.-J.; Mei, T.-S.; Yu, J.-Q. *Angew. Chem., Int. Ed.* **2008**, *47*, 6452–6455. (f) Vickers, C. J.; Mei, T.-S.; Yu, J.-Q. *Org. Lett.* **2010**, *12*, 2511–2513. (g) Mei, T.-S.; Wang, D.-H.; Yu, J.-Q. *Org. Lett.* **2010**, *12*, 3140–314. For a review, see: (i) Giri, R.; Yu, J.-Q. In *e-EROS, Encyclopedia of Reagents for Organic Synthesis*; John Wiley & Sons, Ltd.: 2008; DOI: 10.1002/047084289X.rn00915.

yield **4a** in 88% yield (entry 15). We also checked that neither iodine nor $PhI(OAc)_2$ alone was capable of promoting this transformation under otherwise identical conditions. It is interesting to note that products resulting from the alternative pathway, involving the participation of MeCN, were not observed.[19]

Table 1. Survey of Reaction Conditions



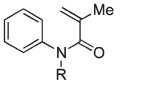
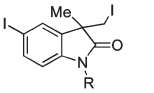
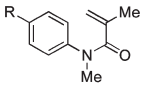
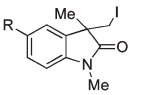
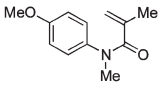
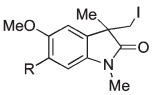
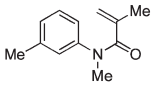
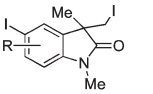
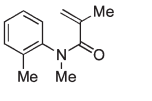
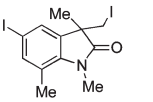
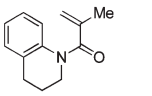
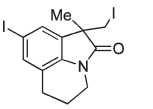
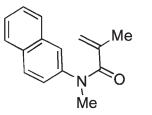
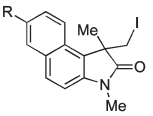
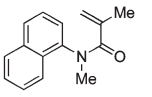
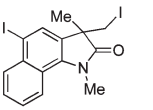
entry	iodonium source	solvent	yield (%)[a]
1	I_2	AcOH[c]	0
2	ICl	AcOH	Trace
3[b]	IPy_2BF_4/HBF_4	CH_2Cl_2	0
4	IBX/I_2	AcOH	34
5	$PhI(OAc)_2/I_2$	AcOH	66
6	$PhI(OCOCF_3)_2/I_2$	AcOH	58
7	$AgOAc/I_2$	AcOH	62
8	$PhI(OAc)_2/I_2$	TFA	40
9	$PhI(OAc)_2/I_2$	MeOH	N.R.
10	$PhI(OAc)_2/I_2$	CH_2Cl_2	31
11	$PhI(OAc)_2/I_2$	THF	Trace
12	$PhI(OAc)_2/I_2$	EtOAc	24
13[c]	$PhI(OAc)_2/I_2$	DCE	47
14	$PhI(OAc)_2/I_2$	Dioxane	Trace
15	$PhI(OAc)_2/I_2$	CH_3CN	88
16	$PhI(OAc)_2/I_2$	DMF	Trace
17	$PhI(OAc)_2/I_2$	DMSO	18

[a] Isolated yield. [b] Reaction performed at 0 °C. [c] Reaction performed at 80 °C.

With the optimum conditions [$PhI(OAc)_2$ (1.5 equiv), I_2 (1.5 equiv), in CH_3CN at rt] in hand, we next examined the scope of this process, and the results are presented in Tables 2 and 3. Use of a tertiary amide was mandatory to ensure the occurrence of the iodo-carbocyclization as no oxindole was formed in the case of *N*-phenylmethacrylamide (entry 1, Table 2). The *N*-benzyl derivative afforded oxindole **4c** in 74% yield. It is worth mentioning that the benzyl residue did not participate in the cyclization as no 1,2-dihydroisoquinolin-3(4*H*)-one was observed. The presence of an electron-donating or -withdrawing group at the *para*-position of anilides was well tolerated (entries 3–6). However, 3 equiv of $PhI(OAc)_2/I_2$ were required to achieve full conversion of 4-cyano anilide (entry 4). Except for the 4-methoxy-substituted anilides, no additional iodination of the aromatic ring was observed. When *N*-*meta*-tolylmethacrylamide was employed, an inseparable mixture of regioisomers **4g** and **4g′** (1.4:1 ratio) was isolated in 81% overall yield in favor of the 6-substituted oxindole (entry 7). *Ortho*-substitution was also compatible as demonstrated by the formation of **4h** (entry 8). Cyclization of

(19) Yeung, Y.-Y.; Gao, X.; Corey, E. J. *J. Am. Chem. Soc.* **2006**, *128*, 9644–9645.

Table 2. Scope of the Iodo-Carbocyclization: Substitution at the Anilines[a]

entry	substrate (**3**)	product (**3**)	yield (%)[b]
1			**4b**, R = H, 0
2			**4c**, R = Bn, 74
3			**4a**, R = I, 96.
4			**4d**, R = CN, 67[c]
5			**4e**, R = Me, 67
6[d,e]			**4f**, R = H **4f'**, R = I 68 (4.7/1)
7			**4g**, R = 6-Me, **4g'**, R = 4-Me, 81 (1.4/1)
8			**4h**, 68
9[c]			**4i**, 75
10			**4j**, R= H, **4j'**, R= I, 98 (1/1)
11			**4k**, 75

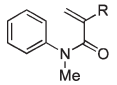
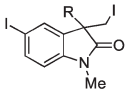
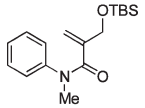
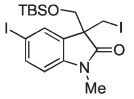
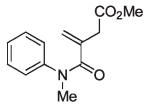
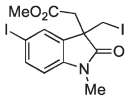
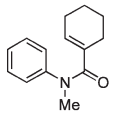
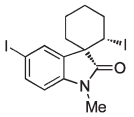
[a] General conditions: $PhI(OAc)_2$ (1.5 equiv), I_2 (1.5 equiv), CH_3CN, rt. [b] Isolated yield. [c] $PhI(OAc)_2$ (3 equiv), I_2 (3 equiv), CH_3CN, rt. [d] $PhI(OAc)_2$ (1.0 equiv), I_2 (1.0 equiv) at 0 °C. [e] 14% of starting marterial was recovered.

a tetrahydroquinoline derivative furnished tricyclic oxindole **4j** in 75% yield (entry 9). A regioselective reaction was also observed with the α- or *β*-naphthylanilide as shown in entries 10 and 11 (Table 2).

Variation at the acrylamide residue was next evaluated (Table 3). *n*-Butyl, *i*-propyl, phenyl, and benzyl groups were tolerated at the α-position of the acrylamide providing the corresponding iodooxindoles in yields ranging from 59 to 83% (entries 1–4, Table 3). Whereas iodination was observed on the aniline aromatic ring in each case, phenyl and benzyl groups at the α-position remained untouched (entries 3 and 4). Silyloxyl and methyl ester groups were compatible with the reaction conditions as illustrated with the synthesis of compounds **4p** and **4q** (entries 5 and 6). α,*β*-Disubstituted *N*-phenylacrylamides were also subjected to the process affording the spirooxindoles in 40% yield (entry 7, Table 3). The reaction was, however, limited to the synthesis of 3,3′-disubstitued oxindoles as no desired product was observed for *N*-phenylacrylamide (data not shown).

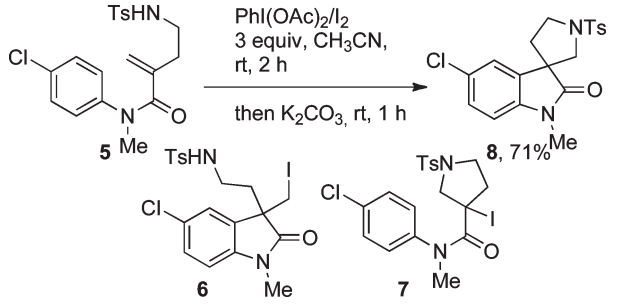
We finally evaluated the reactivity of anilide **5** bearing a tosyl-protected alkylamine side chain at the α-position of the acrylamide. Two possible reaction pathways, namely,

Table 3. Scope of the Iodo-Carbocyclization: Substitution at the Acrylates[a]

entry	substrate (**3**)	product (**4**)	yield (%)[b]
1			**4l**, R = *n*-Bu, 83
2[c]			**4m**, R = *i*-Pr, 59
3			**4n**, R = Ph, 81
4			**4o**, R = Bn, 76
5			**4p**, 52
6[c]			**4q**, 47
7			**4r**, 40[d]

[a] General conditions: $PhI(OAc)_2$ (1.5 equiv), I_2 (1.5 equiv), CH_3CN, rt. [b] Isolated yield. [c] $PhI(OAc)_2$ (3 equiv), I_2 (3 equiv), CH_3CN, rt. [d] Only one diasteroisomer was isolated. The stereochemistry of **4r** was tentatively assigned based on a mechanistic hypothesis.

Scheme 2. One-Step Synthesis of Spirooxindole



iodo-arylation and iodo-sulfonamidation,[20] could occur leading to oxindole **6** and pyrrolidine **7**, respectively. Both **6** and **7** could, in principle, be converted to the biologically relevant spiropyrrolidinyloxindole **8** (Scheme 2).[21] Eventually, treatment of an acetonitrile solution of **5** with 3 equiv of $PhI(OAc)_2/I_2$ followed by addition of K_2CO_3 afforded directly the spirooxindole **8** in 71% yield. When the addition of K_2CO_3 was omitted, oxindole **6** was isolated in excellent yield at the expense of **7**, indicating that the iodo-arylation dominated over the alternative iodo-sulfonamidation under these conditions.

In summary, we have developed a novel metal-free synthesis of 3,3′-disubstituted oxindoles via an iodine monoacetate-promoted iodoarylation of anilides. The salient features of the present halonium-induced cyclization are as follows: (a) it involves, for the first time, an electron-deficient olefin; (b) it proceeds via a unique 5-*exo*-trig cyclization mode in contrast to the more common 6-*endo*-trig mode observed for most of the halonium-induced cyclizations of 1,5-dienes. While a few metal-catalyzed cyclizations of anilides involving a C−H functionalization step have been developed for the synthesis of oxindoles, we believe that the present metal-free conditions provided an attractive alternative to access this important type of heterocycle. Efforts aiming at understanding the reaction mechanism are ongoing.[22]

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Supporting Information Available. Supporting Information for this article, including experimental procedures, product characterization. and copies of the ^1H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

(20) For 5-*endo*-trig iodo-sulfonamidation for the synthesis of pyrrolidines, see: (a) Jones, D. A.; Knight, D. W.; Hibs, D. E. *J. Chem. Soc., Perkin Trans.* **2001**, *1*, 1182–1203. (b) Amjad, M.; Knight, D. W. *Tetrahedron Lett.* **2006**, *47*, 2825–2828.

(21) Jaegli, S.; Vors, J.-P.; Neuville, L.; Zhu, J. *Tetrahedron* **2010**, *66*, 8911–8921.

(22) One reaction pathway involved a 1,4-addition of an iodine radical to the conjugated double bond followed by radical cyclization onto the aromatic ring. However, the following results seemed to be against this proposal in our case: (i) cyclization of **3a** took place readily in the dark to afford **4a** in a similar yield; (ii) addition of benzoquinone did not inhibit the reaction; (iii) although yield remained moderate, the cyclization of (*Z*)- and (*E*)-*N*-2-dimethyl-*N*-phenylbut-2-enamide was stereospecific affording two distinct diastereomers (cf. Supporting Information). For radical based cyclization to oxindoles, see: (a) Teichert, A.; Jantos, K.; Harms, K.; Studer, A. *Org. Lett.* **2004**, *6*, 3477–3480. (b) Murphy, J. A.; Tripoli, R.; Khan, T. A.; Mali, U. W. *Org. Lett.* **2005**, *7*, 3287–3289.