Hypervalent Iodine Reagents

DOI: 10.1002/anie.201206420

Defined Hypervalent Iodine(III) Reagents Incorporating Transferable Nitrogen Groups: Nucleophilic Amination through Electrophilic Activation**

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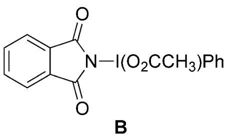
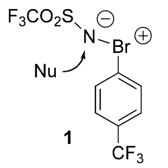
Direct oxidative amination reactions of hydrocarbons are of high synthetic importance as they have no or little precedence in nature.[1] Processes of this type that proceed under metal-free conditions are particularly desirable owing to their environmental benigness and practicability. In principle, hypervalent iodine(III) reagents with their high oxidation potential are a promising concept for oxidative amination.[2] In examples in the area, mainly by Domínguez and co-workers, a reagent combination consisting of amides and $PhI(O_2CCF_3)_2$ was used; an intermediate **A** with an I−N bond was postulated, which generates an electrophilic nitrogen source upon heterolytic dissociation.[3] Despite their obvious synthetic utility, little information has been uncovered on the structural basis of the intermediary iodine reagents.

$NR'R{-}I(O_2CCF_3)Ph$

A



B



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Recently, a series of metal-free amination reactions of compounds with unfunctionalized carbon–hydrogen bonds have become available. These include direct aromatic amination,[4] and the oxidative transfer of phthalimide to benzylic positions and aromatic rings.[5] The involvement of intermediate **B** with an iodine–nitrogen single bond as a precursor to nitrogen radicals or electrophiles has been suggested in the latter cases. However, definite structural proof could not be obtained for this putative intermediate.[6] In a striking accomplishment, Ochiai isolated the hypervalent bromine(III) reagent **1**, which is attacked by alkenes at the σ* N−Br orbital and even undergoes direct C−H amination of alkanes at room temperature.[7,8]

In general, hypervalent iodine(III) species containing I−N single bonds are rare.[9,10] More importantly from a synthetic standpoint, isolated hypervalent iodine(III) reagents bearing a defined I−N single bond with a transferable nitrogen group for metal-free amination reactions of hydrocarbons are extremely scarce and no general reactivity has been described so far. In recent work,[11] we reported unusual metal-free diamination, and allylic and acetylenic amination reactions based on a new hypervalent iodine(III) reagent of the type $PhI(OAc)N(SO_2R)_2$. We now describe the synthesis and isolation of unprecedented hypervalent iodine species of the formula $PhI[N(SO_2R)_2]_2$, discuss their formation and their solid-state and solution structures, and report unparalleled chemical transformations based on electrophilic activation/nucleophilic amination with these reagents.

We recently found that iodosobenzene diacetate undergoes protonolysis in the presence of bistosylimide leading to loss of acetic acid and to immediate formation of the monomeric species **2a**.[11a] However, we noticed that for the diamination of styrene as a standard transformation, the isolated compound **2a** promoted only a slow reaction. Moreover, addition of a second equivalent of bistosylimide is required for a quantitative transformation. As a consequence, we anticipated that **2a** is not the active reagent, but rather a precursor to it. Indeed, in the presence of water, **2a** is converted into the new μ-oxo-bridged compound **3** (Scheme 1). This product is also obtained directly from iodosobenzene diacetate upon treatment with bistosylimide and water. This formation of **3** is a fast process as monitored by in situ IR spectroscopy. Characteristic IR bands at $1714\,cm^{-1}$ confirm the presence of **2a** as a short-living intermediate during the formation of **3**.[12,13]

Compound **3** is an active reagent in the diamination of styrene; however, as only two bistosylimido units are present, it gives a maximum yield of 50% together with iodosobenzene as the remaining iodine(III) species. Treatment of **3** with an additional two equivalents of bistosylimide leads to further chemical transformation and to the clean formation of the new monomeric iodine(III) compound **4**, which incorporates two bisimido groups (Scheme 1).

The solid-state structure of **4** is depicted in Figure 1.[12] It displays comparably short I−N distances of 2.210 Å, owing to the required stabilization of the electrophilic iodine center. Compound **4** indeed represents the elusive active reagent in the diamination of alkenes.[11a–c] When the initial conversion of styrene was monitored, the relative rate of the reaction

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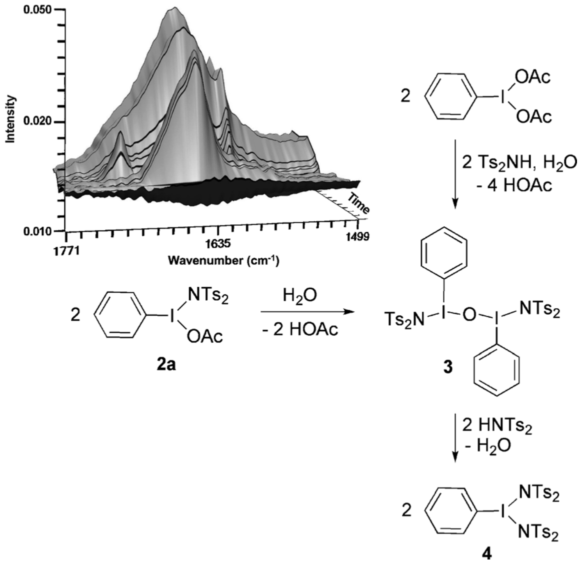
[**] We thank Fundación ICIQ and the Spanish Ministerio de Economía (CTQ2011-25027) for financial support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201206420.



Scheme 1. Sequential transformation of iodine(III) compounds **2a** and **3** into reagent **4**, and formation of **3** as indicated by in situ IR spectroscopy.

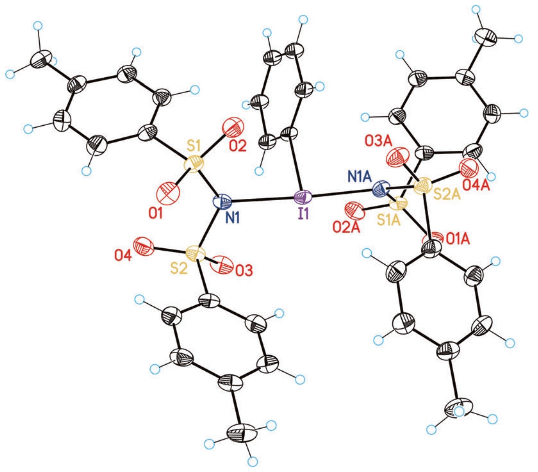
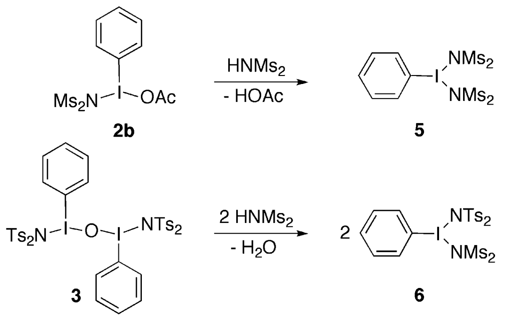


Figure 1. X-ray crystal structure of **4**; ellipsoids at 50% probability. Selected bond lengths [Å] and angles [°]: I1–C15 2.117(17), I1–N1 2.210(4), I1–N1A 2.210(4); C15-I1-N1 88.37(10), N1-I1-N1A 176.7 (2).

with **4** was found to be three times higher than that with **3**.[13] The superior reactivity of $PhI(NTs_2)_2$ (**4**) over its precursors **2** and **3** can also be considered to be the result of enhanced electrophilicity at the central iodine(III) atom owing to the presence of two less stabilizing imido ligands.

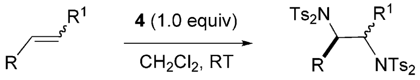
The synthesis of **4** from **3** proceeds quantitatively through protonolysis and thus is again a pK_a-driven pathway. In a related transformation, compound $PhI(NMs_2)_2$ (**5**) is generated directly from the corresponding precursor **2b** (Scheme 2). Because of its basic μ-oxo bridge, compound **3** can serve as a general precursor for protonolysis events to generate mixed bisimido iodine(III) compounds. For example, the compound $PhI(NTs_2)NMs_2$ (**6**) is obtained from the corresponding protonolysis of **3** with bismesylimide.



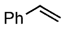
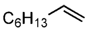
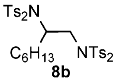
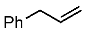
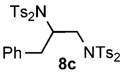
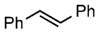
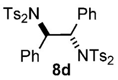
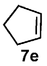
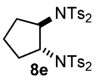
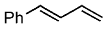
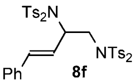
Scheme 2. Synthesis of bisimido iodine(III) reagents **5** and **6**.

Isolated compound **4** is an excellent reagent for the diamination of alkenes (Table 1). It promotes rapid and productive reactions at room temperature within minutes that significantly surpass earlier examples relying on the in situ formation of the reagent, which usually requires significantly longer reaction times and partially harsher conditions.[11b,c] Representative examples include the diamination of styrene (**7a**), 1-octene (**7b**), allyl benzene (**7c**) stilbene (**7d**), and cyclopentene (**7e**). The regioselective diamination of butadiene **7f** now also proceeds at room temperature. The robustness of the new process was further demonstrated by diamination of **7a** on a 20 mmol scale (Table 1, entry 2).

Table 1: Diamination reactions with isolated reagent **4**.[a]

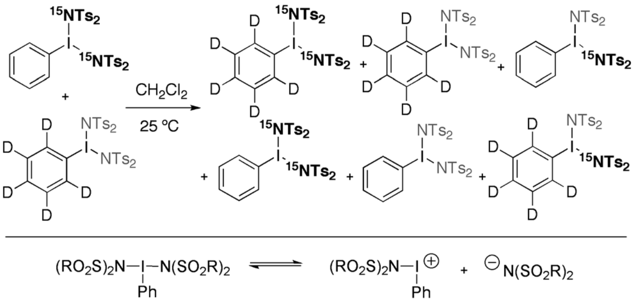


7a-f **8a-f**

Entry	Substrate	Product	t [min]	Yield [%][b]	Previous best conditions
1	 **7a**	 **8a**	25	80	$PhI(OAc)_2$/ 2 $HNTs_2$, RT, 12 h, 80%[11b]
2[c]			30	78[d]	
3	 **7b**	 **8b**	50	82	$PhI(OAc)_2$/ 2 $HNTs_2$, 50°C, 12 h, 80%[11b]
4	 **7c**	 **8c**	90	90	$PhI(OAc)_2$/ 2 $HNTs_2$, 50°C, 12 h, 90%[11b]
5	 **7d**	 **8d**	240	66	$PhI(OAc)_2$/ 2 $HNTs_2$, 50°C, 12 h, 56%[11b]
6	 **7e**	 **8e**	300	72	$PhI(OAc)NTs_2$/ $HNTs_2$, 45°C, 96 h, 46%[11b]
7	 **7f**	 **8f**	90	91	$PhI(OAc)NTs_2$/ $HNTs_2$, RT, 12 h, 75%[11c]

[a] 0.2 mmol scale. [b] Yield of product isolated after purification. [c] Reaction at a 20 mmol scale. [d] Yield of product isolated after a single recrystallization from MeOH.

In investigations of the behavior of reagent **6** in the diamination of styrene all four possible diamination products were obtained.[13] This suggests that the individual bissulfonylimide groups in **4** and **5** should be labile and exchangeable in solution. To further illustrate this finding, isotopically labeled derivatives of **4** with a ^{15}N-labeled bistosylimide and a pentadeuterated phenyl substituent were prepared. When the two species were mixed at room temperature, apparently completely statistical equilibration of all nitrogen groups took place at the iodine centers (Scheme 3). An MS experiment confirmed this observation through the identification of all four corresponding cationic iodine fragments $[PhINTs_2]^+$, $[PhI^{15}NTs_2]^+$, $[C_6D_5INTs_2]^+$, and $[C_6D_5I^{15}NTs_2]^+$.[13]

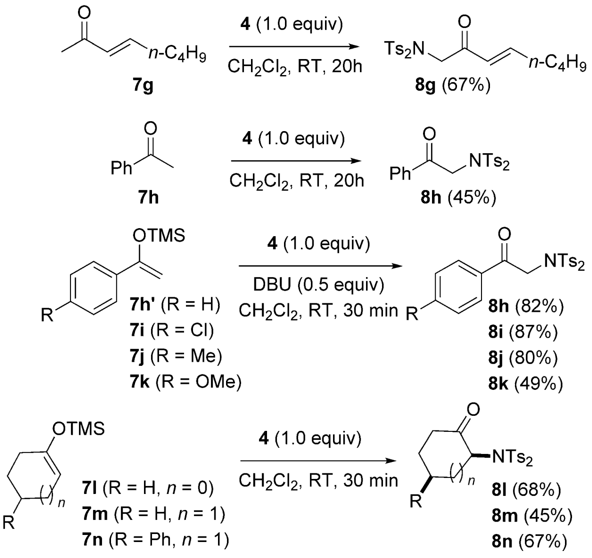


Scheme 3. Dynamic behavior of bissulfonylimido groups in solution.

As a result, compounds **4**–**6** are characterized by the enhanced electrophilicity of the iodine(III) center, which accelerates interaction with the π-system of substrates **7**. This is combined with the corresponding nucleophilic behavior of the free bistosylimide (Scheme 3, bottom). This is significantly different from the previously mentioned pathways for iodine(III)-mediated aminations through **A** or **B**, which are based exclusively on electrophilic character at nitrogen or suggest the involvement of radical pathways. In contrast, in the new complexes of type **4** the bissulfonylimides retain their nucleophilicity and therefore induce electrophilic character at iodine, which in addition to the established diamination reactions from Table 1 allows for new amination chemistry at comparably low temperatures and under mild conditions.

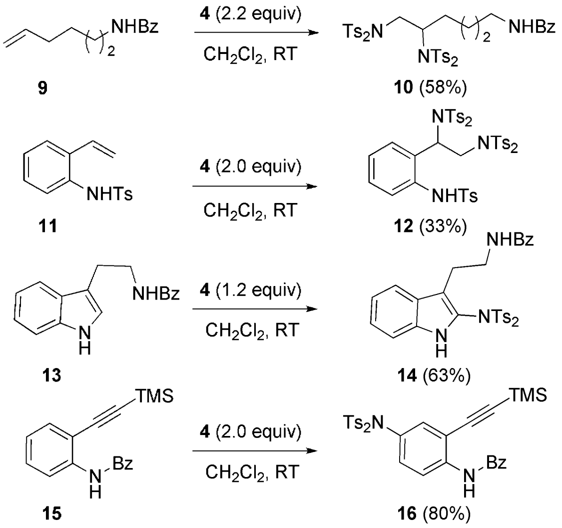
For example, unprecedented α-amination reactions of ketones were discovered in the oxidation of the α,β-unsaturated ketone **7g** and acetophenone **7h** with **4** (Scheme 4), which presumably proceed through the corresponding enol form. Indeed, when the preformed silyl enol ethers **7h′**–**k** are used, the corresponding α-aminated acetophenones **8h**–**k**[12] are formed within minutes at room temperature. To demonstrate the utility of these products as synthetic building blocks, the related α-amination between **7h′** and $PhI(NMsTs)_2$ was performed and the resulting aminated acetophenone could be converted into the corresponding monotosylated aminoalcohol in two steps.[13]

Importantly, only the use of isolated reagent **4** provides the neutral conditions essential for successful amination, as reagent combinations consisting of $PhI(OAc)_2$ and $HNTs_2$ liberate acid and lead to predominant cleavage of the TMS enol ethers. The α-amination reaction is further successful for cyclic enol ethers **7l**–**n**, which give the corresponding α-aminated ketones **8l**–**n**. These transformations are of interest as they serve to differentiate the nucelophilic amination reactivity of **4** from the putative reagent $PhI(N_3)_2$.[14] The latter is a source of azide radicals and gives exclusive allylic azidonation in the oxidation of the related TIPS enol ethers. For the formation of α-azido ketones, the presence of TEMPO at −78 °C and significantly higher reaction times of up to 24 h are required.[16]



Scheme 4. Iodine(III)-promoted α-amination of ketones.

The unique potential of reagent **4** is further demonstrated by the following examples of metal-free amination reactions (Scheme 5). Importantly, the reagent combinations $PhI(OAc)_2/2\,HNTs_2$ and $PhI(OAc)NTs_2/HNTs_2$ were ineffective in these cases, and other hypervalent-iodine oxidants gave completely different products, if any.[13] First, oxidation of alkene **9** results in complete intermolecular diamination to



Scheme 5. Unprecedented metal-free amination reactions of **4** overriding intramolecular cyclization.

give **10** overcoming any preference for intramolecular piperazine formation.[16] More strikingly, the 2-vinyl aniline **11** undergoes selective intermolecular diamination to give **12**. A potential indole cyclization was never observed under these conditions, as had occurred with other iodine(III) reagents.[13] The tryptamine derivative **13** was found to undergo another unprecedented amination reaction to provide the 2-aminated indole **14**, in which again preferential intermolecular reactivity over intramolecular reactivity was observed.[17,18] Finally, the enhanced electrophilicity of **4** provides additional unexpected reactivity in a new oxidation of 2-acetylenyl aniline **15** at room temperature. In this case, the expected common reactions, oxidation of the alkyne or oxidatively induced cyclization, do not take place. Instead, an intermolecular regioselective aromatic oxidation yields **16** in a reaction that may be considered the aza analogue[19] of a Kita oxidation.

We have explored the nature of the active iodine(III) species in metal-free amination reactions. These reagents were isolated for the first time and identified to be bisimido iodine(III) compounds $PhI[N(SO_2R)_2]_2$. Their unprecedented reactivity enables several new transformations, and defined hypervalent iodine(III) reagents incorporating transferable nitrogen groups are now available for the development of additional direct metal-free amination reactions.

Received: August 9, 2012
Revised: October 1, 2012

Keywords: amides · amination · iodine(III) reagents · nucleophilicity · oxidation

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[11] a) C. Röben, J. A. Souto, Y. González, A. Lishchynskyi, K. Muñiz, *Angew. Chem.* **2011**, *123*, 9650; *Angew. Chem. Int. Ed.* **2011**, *50*, 9478; b) J. Souto, Y. González, A. Iglesias, D. Zian, A. Lishchynskyi, K. Muñiz, *Chem. Asian J.* **2012**, *7*, 1103; c) A. Lishchynskyi, K. Muñiz, *Chem. Eur. J.* **2012**, *18*, 2212; d) J. A.

Souto, D. Zian, K. Muñiz, *J. Am. Chem. Soc.* **2012**, *134*, 7242; e) J. A. Souto, P. Becker, A. Iglesias, K. Muñiz, *J. Am. Chem. Soc.* **2012**, *134*, 15505.

[12] CCDC 811767 (**3**), 893042 (**4**), 902658 (**8i**), 862030 (**14**), and 893041 (**16**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[13] Further details are included within the Supporting Information.

[14] While compound **4** is stable under laboratory conditions and can be handled conveniently, $PhI(N_3)_2$ must be generated in situ from PhIO and $TMSN_3$ and is unstable above −30°C: a) M. Arimoto, H. Yamaguchi, E. Fujita, Y. Nagao, M. Ochiai, *Chem. Pharm. Bull.* **1989**, *37*, 3221; b) M. Arimoto, H. Yamaguchi, E. Fujita, M. Ochiai, Y. Nagao, *Tetrahedron Lett.* **1987**, *28*, 6289; c) J. Ehrenfreund, E. Zbiral, *Tetrahedron* **1972**, *28*, 1697. The superiority of **4** over $PhI(N_3)_2$ is further evidenced by its isolation, storage, and large-scale application (Table 1, entry 2). For the corresponding radical-mediated bisazodination reactions see also: d) P. Magnus, M. B. Roe, *Tetrahedron Lett.* **1996**, *37*, 303; e) R. Chung, E. Yu, C. D. Incarvito, D. J. Austin, *Org. Lett.* **2004**, *6*, 3881.

[15] a) P. Magnus, J. Lacour, P. A. Evans, M. B. Roe, C. Hulme, *J. Am. Chem. Soc.* **1996**, *118*, 3406; b) P. Magnus, J. Lacour, *J. Am. Chem. Soc.* **1992**, *114*, 767; c) P. Magnus, J. Lacour, *J. Am. Chem. Soc.* **1992**, *114*, 3993; d) P. Magnus, M. B. Roe, C. Hulme, *Chem. Commun.* **1995**, 263.

[16] For examples of $PhI(OAc)_2$-mediated intramolecular formation of pyrrolidines from alkenes: a) B. M. Cochran, F. E. Michael, *Org. Lett.* **2008**, *10*, 5039; b) H. M. Lovick, F. E. Michael, *J. Am. Chem. Soc.* **2010**, *132*, 1249; c) for an elegant enantioselective version: U. Farid, T. Wirth, *Angew. Chem.* **2012**, *124*, 3518; *Angew. Chem. Int. Ed.* **2012**, *51*, 3462.

[17] For recent examples of cyclization reactions of tryptamine derivatives with hypervalent iodine: a) D. Kajiyama, T. Saitoh, S. Yamaguchi, S. Nishiyama, *Synthesis* **2012**, 1667; with halonium sources: b) O. Lozano, G. Blessley, T. Martinez del Campo, A. L. Thompson, G. T. Giuffredi, M. Bettati, M. Walker, R. Borman, V. Gouverneur, *Angew. Chem.* **2011**, *123*, 8255; *. Chem. Int. Ed.* **2011**, *50*, 8105; c) J. Kim, M. Movassaghi, *J. Am. Chem. Soc.* **2010**, *132*, 14376; d) P. Ruiz-Sanchis, A. S. Svetlana, F. Albericio, M. Alvarez, *Chem. Eur. J.* **2011**, *17*, 1388; with selenium sources: A. J. Oelke, D. J. France, T. Hofmann, G. Wuitschik, S. V. Ley, *Angew. Chem.* **2010**, *122*, 6275; *Angew. Chem. Int. Ed.* **2010**, *49*, 6139.

[18] The observed 2-amination is also an interesting contrast to a recent investigation on the oxidation of 3-methylindole with $PhI(OAc)_2$: Y.-X. Li, H.-X. Wang, S. Ali, X.-F. Xia, Y.-M. Liang, *Chem. Commun.* **2012**, *48*, 2343.

[19] For an intramolecular version: L. M. Pardo, I. Tellitu, E. Domínguez, *Tetrahedron* **2010**, *66*, 5811.