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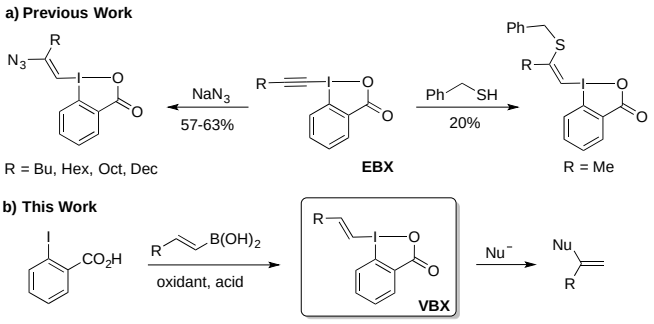
Synthesis, Characterization and Unusual Reactivity of Vinylbenziodoxolones – Novel Hypervalent Iodine Reagents

Elin Stridfeldt,[a] Alexandra Seemann,[a] Marinus J. Bouma,[a] Chandan Dey,[a] Anne Ertan[b] and Berit Olofsson[a]*

Abstract: A novel type of hypervalent iodine(III) reagents, vinylbenziodoxolones (VBX), has been synthesized in a one-pot reaction from 2-iodobenzoic acid. VBX is bench stable, has been thoroughly characterized and the cyclic structure is supported by X-ray analysis. The reactivity of VBX was investigated in vinylation of nitrocyclohexane, and delivered vinylated products with opposite regioselectivity compared to acyclic vinyl(aryl)iodonium salts. The reagents could become a powerful tool in vinylation reactions under both metal-free and metal-catalyzed conditions.

Hypervalent iodine compounds are well-known for their use as mild and selective oxidants, and have recently proved to be versatile in a wide variety of other transformations.[1] Iodine(III) reagents with two carbon ligands are nowadays frequently employed as group transfer reagents under both metal-catalyzed and metal-free conditions.[2] One reason for their gain in popularity is the development of cyclic benziodoxol(on)es, which tend to be more stable than their acyclic counter-parts.[2b,3] The use of the benziodoxol(on)e core has enabled the synthesis of reagents such as trifluoromethylbenziodoxol(on)es (Togni's reagents) and azidobenziodoxolones, which are too unstable to be isolated as acyclic structures.[4] Compounds that are stable as iodonium salts, such as diaryliodonium salts and alkynyl(aryl)iodonium salts, have also been obtained as benziodoxolones.[2b] Ethynylbenziodoxolones (EBX) and cyano-benziodoxolones have been demonstrated to outperform the acyclic alkynyl and cyano salts, respectively, in several applications.[5]

Vinyl(aryl)iodonium salts have recently been successfully applied in copper-catalyzed reactions,[6] but the reactivity in metal-free reactions is rather complex, and the mechanisms vary with the iodonium salt used.[2d,7] We envisioned better control of the reactivity in a benziodoxolone structure, as observed with alkynyl salts *vs.* EBX. To the best of our knowledge, vinylbenziodoxolones (VBX) have never been investigated as reagents. In fact, this compound class has only been reported as products from addition reactions to alkynylbenziodoxolones (Scheme 1a).[8] Our group has a long-term interest in efficient one-pot routes to iodine(III) reagents from iodoarenes,[9] and investigated this approach to synthesize the unexplored VBX. The strategy proved to be successful, and herein we report the first one-pot synthesis, X-ray structure and preliminary reactivity screen of VBX (Scheme 1b).



Scheme 1. Synthesis and reactivity of VBX.

Vinyl(aryl)iodonium salts are commonly synthesized by coupling a pre-formed iodine(III) reagent with a vinyl source,[2d] usually employing (diacetoxyiodo)benzene with vinylboronic acids[10] or iodosylbenzene with alkenylsilanes.[11] A one-pot procedure from iodoarenes and terminal alkynes was reported utilizing FXeOTf,[12] and our group discovered a one-pot synthesis from iodobenzene, TMS-phenylacetylene and *m*CPBA.[9h] Benziod-oxolones are often synthesized in several steps from 2-iodobenzoic acid, which is oxidized to hydroxybenziodoxolone and then coupled with a suitable regent.[2b,13] We recently published one-pot syntheses of both alkynyl salts and alkynylbenziodoxolones starting from 2-iodobenzoic acid and either terminal alkynes or alkynylboronic esters.[9b,h]

Our envisioned synthesis of VBX was investigated starting from 2-iodobenzoic acid (**1**), which was oxidized with *m*CPBA in the presence of an acid, and subsequently treated with (*E*)-styrylboronic acid (**2a**, Table 1).[14] To our delight, the reaction was successful both in the presence of tosic acid and triflic acid, delivering the acyclic vinyliodonium salts **5a** (X= OTs or OTf) that could be isolated by precipitation in diethyl ether. Salts **5a** were treated with aqueous sodium bicarbonate to yield the cyclized vinylbenziodoxolone **6a** (entries 1-2).[15] The use of $BF_3{\cdot}OEt_2$ only gave minor amounts of product together with inseparable by-products (entry 3). A 15 min oxidation time (t_1) was sufficient, and longer coupling time (t_2) proved indifferent (entries 4-5).

The pinacol ester **3a** could be used instead of boronic acid **2a**, whereas the silyl reagent **4a** only gave traces of product together with unidentified by-products (entries 6-7). Importantly, the yield was maintained upon significantly reduced reaction times t_1 and t_2 and decreased amount of boronic acid **2a** (entries 8-10). Addition of TfOH and **2a** at 0 °C slightly increased the yield of **6a** (entry 11).

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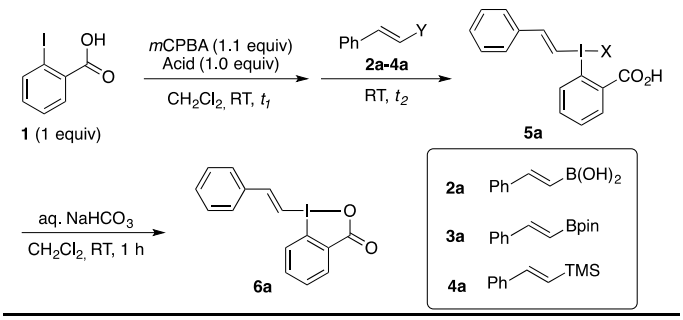
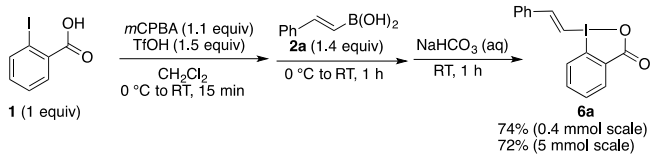
Table 1. Optimization of the synthesis of VBX **6a**.[a]



Entry	Acid	t_1	**2a-4a** (equiv)	t_2 (h)	Yield of **6a** (%)[b]
1	$TsOH·H_2O$	17 h	**2a** (2.0)	2	36
2	TfOH	17 h	**2a** (2.0)	2	69
3	$BF_3·OEt_2$	17 h	**2a** (2.0)	2	<10
4	TfOH	2 h	**2a** (2.0)	2	73
5	TfOH	2 h	**2a** (2.0)	17	71
6	TfOH	2 h	**3a** (2.0)	17	59
7	TfOH	2 h	**4a** (2.0)	17	<5
8	TfOH	15 min	**2a** (2.0)	1	69
9	TfOH	15 min	**2a** (1.4)	1	69
10	TfOH	15 min	**2a** (1.1)	1	60
11[c]	TfOH	15 min	**2a** (1.4)	1	73

[a] Reaction conditions: **1** (0.4 mmol), *m*CPBA and acid in CH_2Cl_2 (2 mL) were stirred at RT for time t_1. **2a-4a** was added and the mixture was stirred at RT for time t_2. The solvent was removed and **5a** was precipitated in Et_2O. **5a** was then cyclized in CH_2Cl_2 (2 mL) and saturated $NaHCO_3$ (2 mL) and isolated by extraction with CH_2Cl_2. [b] Isolated yields. [c] TfOH and **2a** added at 0 °C.

We were pleased to see that the synthesis of VBX **6a** could be performed in a one-pot manner without isolation of **5a** (Scheme 2). Significantly, the reaction was easily scaled up to 5 mmol with maintained yield.



Scheme 2. One-pot synthesis of VBX **6a**.

The structure of *(E)*-styrylbenziodoxolone **6a** was compared to other similar compounds by several analytical methods, including ^{13}C NMR (Table 2). The iodine(III) oxidation state of **5a** and **6a** is in accordance with the ^{13}C NMR shift of the *ipso* carbon, which moved considerably downfield in **5a** and **6a** compared to in **1** (entry 1).[16] Similar shifts of the *ipso* carbon have been observed for 1-(phenylethynyl)-1,2-benziodoxol-3(1*H*)-one (Ph-EBX) and the acyclic styryl(phenyl)iodonium tetrafluoroborate **7** (entry 2).[17] The shifts of the vinylic carbons in **6a** are also in agreement with **7** (entry 3)[17b] and the retained *E* configuration in **6a** is indicated by the coupling constant (J = 15.8 Hz in $CDCl_3$).[14] The cyclic structure of **6a** is supported by the ^{13}C NMR shift of the carbonyl carbon at 166.5 ppm, which is in agreement with **Ph-EBX** (entry 4), as well as previously reported vinylbenziodoxolones.[8a,b] Furthermore, the IR absorption of the carbonyl in **6a** at 1609 cm^{-1} is in the same range as known vinyl benziodoxolones[8a,b] and other benziodoxolones.[18]

Table 2. ^{13}C NMR comparison of **1**, **5a**, **6a**, Ph-EBX and **7** (ppm).

Entry	Solvent	peak	**1**	**5a**[a]	**6a**	**Ph-EBX**	**7**
1	CD_3OD	C-I	94.1	114.9	115.5	-	-
2	$CDCl_3$	C-I	94.9	-	115.1	116.2[17a]	110.2[17b]
3	$CDCl_3$	C=C	-	-	154.5 99.7	-	151.6[17b] 95.8[17b]
4	$CDCl_3$	C=O	171.1	-	166.5	166.7[17a]	-

[a] Not soluble in $CDCl_3$.

The benziodoxolone structure of VBX **6a** was unambiguously assigned by X-ray crystallography.[19] The crystals were prepared by layering a solution of **6a** in DMSO with diethyl ether and submitted to single crystal X-ray analysis (Figure 1). The molecular conformation has a distorted T-shape with an O9-I1-C10 angle of 165.8°, which is similar to the reported arylbenziodoxolones and alkynylbenziodoxolones.[17a,20] The bond angle O9-I1-C6 is 72.9° and the C6-I1-C10 angle of 93.7° are also similar to previous reports, as are the bond lengths between I1-C6 of 2.121 (Å) and I1-C10 of 2.100 (Å). The I1-O9 bond distance of 2.51 Å is significantly larger than in alkynylbenziodoxolones, but in similar length as arylbenziodoxolones.[17a,20] This bond length trend is in agreement with the larger *trans* influence exerted by vinyl and aryl groups compared to alkynyl and trifluoromethyl groups.[3,21]

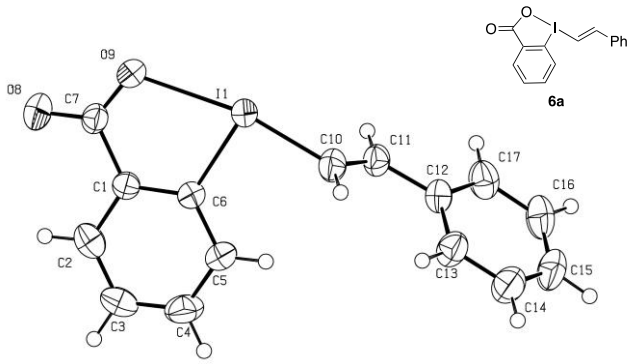
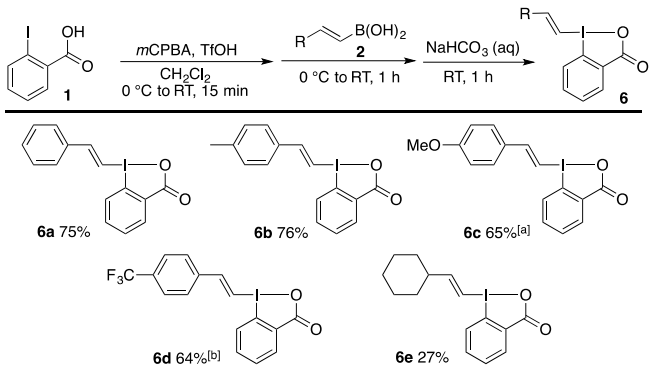


Figure 1. X-ray structure of **6a** with thermal ellipsoids displayed with 50% probability. Selected bond lengths: I1-O9 2.510 Å, I1-C6 2.121 Å, I1-C10

2.100 Å. Selected bond angles: O9-I1-C6 72.9 °, O9-I1-C10 165.8 °, C6-I1-C10 93.7 °.

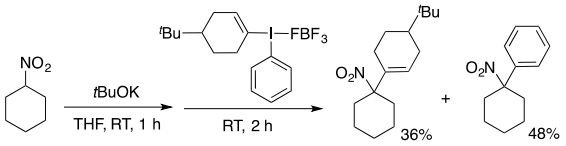
With the structure of VBX **6a** firmly established, other boronic acids **2** were utilized in the one-pot sequence to investigate the scope of the methodology (Scheme 3).[14] Aromatic boronic acids with different *para*-substituents were first investigated, and their electronic properties were found to influence the reaction substantially. Methyl-substituted reagent VBX **6b** was formed in good yield, whereas the more electron-donating methoxy-substituted boronic acid proved too reactive under the reaction conditions, and gave an impure, dark colored product. This could be avoided by employing tosic acid instead of triflic acid, delivering VBX **6c** in good yield. The corresponding acyclic reagent 4-methoxystyryl(phenyl)iodonium tetrafluoroborate was reported to decompose rapidly at room temperature, illustrating the generally observed stabilizing effect of the benziodoxolone core.[22] Synthesis of the electron-deficient trifluoromethyl VBX **6d** could be effected by heating to 50 °C and prolonged reaction time. Unfortunately, aliphatic vinyl boronic acids were less suitable for the developed one-pot conditions, and reactions with cyclohexylboronic acid provided VBX **6e** in moderate yield.



Scheme 3. Scope of one-pot synthesis of VBX **6**. Isolated yields on 0.4 mmol scale, see SI for details. [a] TsOH instead of TfOH. [b] At 50 °C for 3 h.

All reactions were performed without precautions to avoid air or moisture. The VBX products are bench stable and can be stored at room temperature in the dark for at least one month without signs of decomposition. To further support the benziodoxolone structures of products **6b-e** the intermediate acyclic salts **5b-e** were isolated and analyzed for comparison.[14] All acyclic salts were prepared in similar yields as the corresponding benziodoxolones, indicating a quantitative cyclization step.

The reactivity of this novel compound class was subsequently investigated and compared to known reactivity of acyclic vinyliodonium salts. Ochiai and co-workers reported the vinylation of nitrocyclohexane with cyclohexenyl(aryl)iodonium tetrafluoroborates, which delivered a mixture of vinylated and arylated nitrocyclohexanes (Scheme 4).[23]

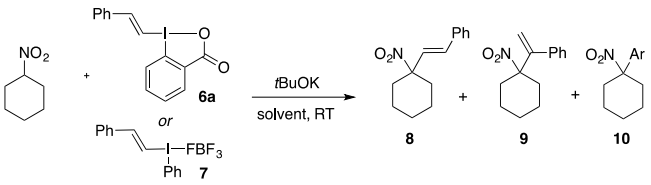


Scheme 4. Ochiai's vinylation of nitrocyclohexane.[23]

While *C*-functionalized nitroalkanes are important scaffolds for further transformations,[24] the reports on *C*-vinylation of nitroalkanes are limited and include the use of stoichiometric amounts of lead reagent,[25] copper-catalyzed carbohalogenation of alkynes[26] or Michael addition to electron-deficient acetylenes.[27] We were hence interested to see whether the VBX reagents would result in chemoselective vinylation and thus provide a useful synthetic route to *C*-functionalized nitroalkanes.

Vinylbenziodoxolone **6a** and the corresponding stryryl-(phenyl)iodonium salt **7** were submitted to Ochiai's conditions,[23] as detailed in Table 3. Reactions with the vinyl(phenyl)iodonium salt **7** delivered a product mixture with vinylated product **8** as the major product, together with minor amounts of the terminal alkene **9** and the phenylated product **10** (entry 1). To our surprise, the major product using VBX **6a** was instead the terminal alkene **9** (entry 2). Furthermore, the reaction proceeded with complete chemoselectivity, i.e. no arylated product **10** was detected by ^{1}H NMR or GC-MS. The reaction conditions were briefly screened,[14] to conclude that increased amount of VBX **6a** (entry 3) or prolonged reaction time (entry 4) did not improve the conversion to **9**. On the other hand, conditions similar to those used in our previously reported arylation of nitrocyclohexane[28] further increased the product ratio **9**:**8** and delivered **9** in a satisfactory yield of 57% (entry 5). Addition of 2 equivalents of the radical scavenger 1,1-diphenylethylene (DPE) did not affect the yield, indication that radicals are not involved in product or byproduct formation.[29]

Table 3. Reactivity difference between VBX **6a** and acyclic salts **7**.[a]



Entry	Solvent	Reagent (equiv)	*t* (h)	Yield (%)[b]		
				8	**9**	**10**
1	THF	**7** (1.1)	18	55	12	<5
2	THF	**6a** (1.1)	18	9	36	n.d.
3	THF	**6a** (2.0)	18	10	37	n.d.
4	THF	**6a** (1.1)	72	8	35	n.d.
5[c]	DME	**6a** (2.0)	72	4	57	n.d.
6[c][d]	DME	**6a** (2.0)	72	4	57	n.d.

[a] Reaction conditions: Nitrocyclohexane (0.24 mmol) and *t*BuOK (1.1 equiv) were stirred at RT for 1 h before addition of **6a** or **7**. [b] ^{1}H NMR yield

calculated using 1,3,5-trimethoxybenzene as internal standard, n.d. = not detected. [c] See SI for details. [d] 2 equiv. DPE added.

The change in product distribution indicates a mechanistic difference between reactions with VBX **6a** and acyclic salt **7**. Styryliodonium salt **7** has been used in metal-free reactions to deliver internal alkenes by thermal solvolysis with acetic acid.[2d,30] The formation of terminal alkenes has been reported in halogenations of **7**, and was assumed to proceed via addition of HBr to *in situ* formed phenylacetylene.[31] This type of mechanism seems unlikely in reactions with nitrocyclohexane, and we are currently investigating the mechanism of the reaction.

In conclusion, a straightforward one-pot synthesis of vinylbenziodoxolones (VBX) has been developed. The cyclic structure is supported by X-ray analysis of the styrylbenziodoxolone **6a**. A preliminary study into the reactivity of this novel class of vinylation reagents showed that reaction between VBX and nitrocyclohexane result in regioselective formation of terminal alkene **9**, which is opposite to the regioselectivity observed with acyclic vinyliodonium salt **7**. The unusual product distribution indicates a different mechanistic pathway, which is currently under investigation in our lab. The related ethynylbenziodoxolones (EBX) have recently proven superior to acyclic alkynyliodonium salts in several applications, and the VBX reagents are currently being explored as powerful reagents in organic synthesis.

Experimental Section

Synthesis of Vinylbenziodoxolones 6

2-Iodobenzoic acid **1** (99.0 mg, 0.40 mmol, 1 equiv) was added to a microwave vial. CH_2Cl_2 (2 mL) was added, followed by *m*CPBA (0.44 mmol, 1.1 equiv). The mixture was cooled to 0 °C and TfOH (0.40-0.60 mmol, 1-1.5 equiv) was added. The solution was stirred at RT for 15 min, and then cooled down to 0 °C. The boronic acid **2** (0.56-0.80 mmol, 1.4-2.0 equiv) was added in one portion and rinsed down with CH_2Cl_2 (0.5 mL) and the mixture was left to stir at RT or 50 °C for 1-3 h. Saturated $NaHCO_3$ (2 mL) was then added and the mixture was stirred vigorously at RT for 1 h. The reaction mixture was diluted with CH_2Cl_2 and H_2O and the layers were separated. The aqueous phase was extracted with CH_2Cl_2 and the combined organic phases were washed with water and brine. The solution was dried over Na_2SO_4, filtered and concentrated. After precipitation with Et_2O the formed solid was filtered off and washed with Et_2O to obtain vinylbenziodoxolone **6** as a white solid.

Acknowledgements

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Keywords: benziodoxolones • hypervalent iodine • structure analysis • synthetic methods • vinylation

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[29] This indicates that the product is not formed via a radical pathway. Further insight into the mechanism cannot be given at this point, but a more detailed study is ongoing in our lab.

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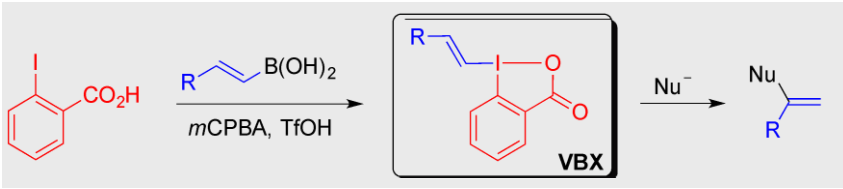
COMMUNICATION



Novel vinylation reagent: Vinylbenziodoxolones (VBX) are stable hypervalent iodine(III) reagents that are efficiently synthesized in a one-pot reaction. The cyclic structure is supported by X-ray analysis. The reactivity of VBX was investigated in *C*-vinylation of nitrocyclohexane, and resulted in opposite regioselectivity compared to vinyl(aryl)iodonium salts.

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