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Access to Vinyl Ethers and Ketones with Hypervalent Iodine Reagents as Oxy-Allyl Cation Synthetic Equivalents

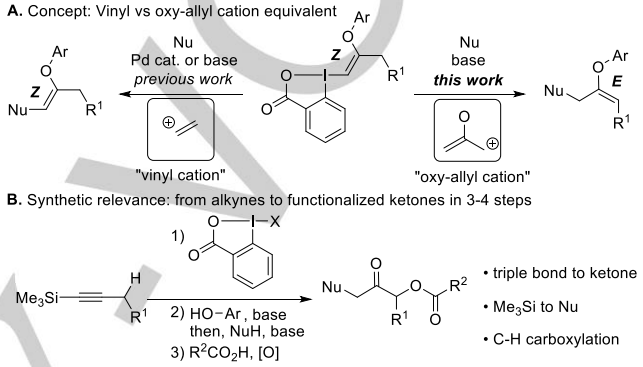
Nina Declas[a] and Jerome Waser*[a]

In the memory of Prof. Dr. Kilian Muñiz

Abstract: We report an Umpolung strategy of enol ethers to generate oxy-allyl cation equivalents based on the use of hypervalent iodine reagents. Under mild basic conditions, the addition of nucleophiles to aryloxy-substituted vinylbenziodoxolone (VBX) reagents, easily available in two steps from silyl alkynes, resulted in the stereoselective formation of substituted aryl enol ethers. The reaction was most efficient with phenols as nucleophiles, but preliminary results were also achieved for C- and N- nucleophiles. In absence of external nucleophiles, the 2-iodobenzoate group of the reagent was transferred. The obtained aryl enol ethers could then be transformed into α-difunctionalized ketones by oxidation. The described "allyl cation"-like reactivity contrast with the well-established "vinyl-cation" behavior of alkenyl iodonium salts.

In standard organic reactions, new bonds are formed between atoms of opposite polarity.[1] First introduced by Seebach,[2] the Umpolung approach -inverting the reactivity of one of the partners- allowed chemical transformations impossible based on the inherent polarity of the reactants. In this context, hypervalent iodine compounds are broadly used in organic synthesis as efficient group transfer reagents via Umpolung of nucleophiles.[3] Enolates, enol ethers and enamines are among the most important nucleophilic synthons in synthetic chemistry.[4] The Umpolung of enolates with hypervalent iodine reagents is well established,[5] but it is only recently that the involved enolonium species could be characterized by Szpilman and co-workers.[6] Nevertheless, controlling transformations involving highly reactive intermediates formed *in situ* is challenging, and an access to stable reagents would be highly desirable.

Cyclic benziodoxol(on)es (BX) reagents are more stable and especially useful for group transfer reactions.[7] Recently, Miyake and co-workers[8] and our group[9a] reported the first synthesis of enol ethers and enamides-based vinyl benziodoxol(on)es (VBX) reagents by the reaction of nucleophiles with ethynyl benziodoxol(on)es (EBX)[10] (Scheme 1A, left). The enhanced reactivity of the hypervalent bond allowed the use of VBX as electrophiles in palladium-catalyzed Stille cross-couplings at room temperature for the formation of aryl, vinyl, alkynyl, and alkyl-substituted *Z*-enamides and enol ethers.[9a] Moreover, they reacted directly with thiol nucleophiles to form thio-enamides, acting as vinyl cation equivalents,[9a] a well established polarityfor alkenyl iodonium salts.[11]



Scheme 1. O-Vinylbenziodoxolones (VBXs) as vinyl and oxy-allyl cation equivalents (A) and application to the synthesis of functionalized ketones (B).

Herein, we report a new mode of reactivity of O-VBX reagents, allowing the Umpolung of enol ethers to give formal oxy-allyl cations instead of vinyl cations (Scheme 1A, right). Oxy-allyl cations have been used as transient electrophilic specie for the reaction with nucleophiles[12] or with dienes in [4 + 3] cycloadditions.[13] They are also formed in the versatile Nazarov cyclization.[14] Enantioselective processes have been recently developed.[15] Access to this type of reactive intermediates from hypervalent iodine reagents has not been reported to the best of our knowledge. Hypervalent iodoallyl intermediates have been proposed in sigmatropic [2,3] and [3,3] rearrangements.[16] Reactive allylic cation intermediates were accessed recently using diazo-substituted hypervalent iodine reagents by Suero.[17] In our work, we now disclose a different approach based on the treatment of O-VBX reagents with base and nucleophiles for the formation of C-O, C-N and C-C bonds in allylic position. The obtained aryl enol ethers were transformed into α-difunctionalized ketones under oxidative conditions (Scheme 1B), resulting in a 3-4 steps synthesis from the corresponding silylated alkynes.

After having successfully used O-VBX reagents as vinyl cation equivalents with thiols,[9a] we attempted to extend this reactivity to phenols as nucleophiles. However, the reaction of O-VBX (**1a**) and *para*-cresol (**2a**) under basic conditions led to the unexpected formation of allyl ether **3a** as main product (Table 1).[18] In 1,2-dimethoxyethane (DME) as solvent with 1.2 equivalents of potassium *tert*-butoxide as base, **3a** could be obtained in 80% yield (entry 1). Other solvents gave a lower yield (See Supporting Information). When various bases were tested, cesium carbonate gave a similar NMR yield as KO*t*Bu, but with higher reproducibility (entry 2),[19] whereas organic bases, such

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Supporting information for this article is given via a link at the end of the document. Raw data for NMR, IR and MS is available at zenodo.org, DOI: 10.5281/zenodo.3894256

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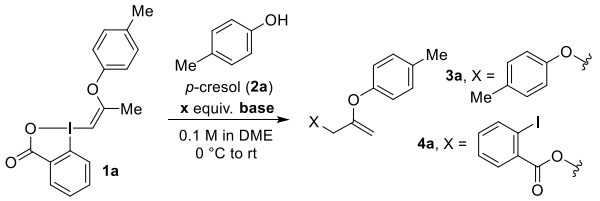
as pyridine and triethylamine gave no reactivity (entries 3-4). O-VBX **1a** was also recovered when performing the reaction without base (entry 5). Incomplete conversion of **1a** was observed when using a catalytic amount or one equivalent of base (entries 6 and 7). In the case of a larger excess of base (entry 8), formation of the allylic ester **4a** resulting from addition of 2-iodo benzoate was increased. In fact, small amounts of **4a** were always observed in this transformation. Allyl ester such as **4a** are valuable building blocks in synthetic chemistry. Furthermore, all the parts of reagent **1a** are incorporated in the product, resulting in high atom economy.[20] Therefore, we optimized the formation of ester **4a** in absence of external nucleophiles (see Supporting Information for details). In presence of 20 mol% anisole as a non-participating nucleophilic additive, **4a** could be obtained as the only product in 65% yield (entry 9).

Table 1. Optimisation of the addition of *p*-cresol (**2a**) to O-VBX **1a**.



Entry	Base	Base equivalents	Yield of **3a** (%)[a]	Yield of **4a** (%)[a]
1	KO*t*Bu	1.20	80	15%
2	Cs_2CO_3	1.20	79	15%
3	Pyridine	1.20	NR	NR
4	Et_3N	1.20	NR	NR
5	none	-	NR	NR
6	Cs_2CO_3	0.20	35	6%
7	Cs_2CO_3	1.00	60	8%
8	Cs_2CO_3	2.00	62	32%
9[b]	Cs_2CO_3	1.20	-	65%

Reactions conditions: Substrate **1a** (0.100 mmol), *para*-cresol (**2a**) (0.100 mmol), base (0.120 mmol) and DME (0.1 M) at 25 °C. NR = No reaction. [a]NMR yield determined by addition of 0.1 mmol of CH_2Br_2 as an internal standard after the reaction. When determined, the yield of **4a** is given in parenthesis. [b]Reaction performed without **2a** in presence of 0.20 equiv. anisole as additive.

To explore the scope of formation of aryl enol ethers and esters, two conditions were used: conditions **A**, starting from isolated O-VBX **1** and conditions **B**, using an one-pot two-step procedure from the corresponding EBX reagent **5** without isolation of the intermediate O-VBX **1** (Scheme 2). For the addition of external nucleophiles to give allyl ethers **3**, method **A** usually gave better yields. For allylic esters **4**, the yields were nearly identical for both methods, and the more practical method **B** was therefore preferred.

The scope of phenol nucleophiles was first investigated (Scheme 2A). On a 0.3 mmol scale, using conditions **A**, substrate **3a** was obtained in 83% yield. When conditions **B** where employed, only 63% yield was observed. The difference came from the larger amount of allyl ester **4a** formed.[21] 4-Bromo- and 4-iodo-phenols afforded the corresponding products **3b** and **3c** in respectively 75% and 73% yields. 4-Methoxyphenol ether **3d** was obtained in a reduced yield of 45%, due to increased formation of ester **4a**. Boronic acid pinacol ester **3e** was formed in 71% yield. A *meta*-methoxy group was also well tolerated (product **3f**). When an unprotected amine-containing substrate was employed, 35% of product **3g** was still obtained, but significant decomposition was observed. Aryl enol ether **3h** bearing an *ortho* ester group was obtained in 89% yield. A sterically highly hindered hydroxyacetophenone still afforded compound **3i** in 43% yield. 2-Naphthol was successfully converted into the corresponding aryl enol ether **3j** in 72% yield.

The scope of the reaction could be extended to more complex phenols (Scheme 2B). Protected tyrosine gave the desired product **3k** in 96% yield. Two natural products containing phenols -capsaicin and estradiol- could be used subsequently in the one-pot protocol **B** to give highly functionalized product **3l** in 41% yield. Under the optimized conditions, the reaction worked best with phenols. Nevertheless, promising results were obtained with several C- and N-nucleophiles (Scheme 2B). Diketone and ketoester-derived products **3m** and **3n** were obtained in 31 and 65% yield respectively, whereas tosyl amide **3o** was isolated in 33% yield.

Having explored the reactivity of various nucleophiles, we turned to the scope of O-VBX reagents with *para*-cresol (**2a**) as nucleophile (Scheme 2C). Propyl-substituted O-VBX **1b** led to formation of allylic ether **3p** in 65% yield with a complete *E*-stereoselectivity.[22] The formation of **3p** also confirmed that the new C-O bond was formed at the position of the iodine atom. A longer alkyl chain was also well tolerated and product **3q** was obtained in 57% yield. A hypervalent iodine reagent bearing a free alcohol could be converted into allylic ether **3r**. Ethers **3s** and **3t** containing a protected alkyne and a phthalimide group could also be accessed. We could also perform this transformation with O-VBX bearing phenol with an iodide in *ortho* position to give products **3u-w** in 44-61% yield. An electron-donating group in *para* position was also well tolerated (products **3x** and **3y**). When the reaction was examined for N-VBX reagent **1l** bearing a sulfonamide group, the product **3z** could be observed by NMR in about 30% yield. However, isolation of the product always led to partial decomposition and isomerization to the more stable internal alkene.

We then examined the synthesis of allyl esters using conditions **B** (Scheme 2D). Primary alkyl chains were well tolerated on the EBX reagents, and products **4b-d** were obtained in good yield (Scheme 6A). EBXs bearing functional groups such as a protected alkyne, a phthalimide, an alkene or a chloride could be converted to the corresponding products **4e-h** in 60% to 82% yield. Halogen substituents were also tolerated. The *ortho*-iodo, *meta*-bromo and pentafluoro, derivates **4i-m** were obtained in 40% to 70% yield. In addition, phenols bearing an electron-donating methoxy group in *para* position or an electron-withdrawing aldehyde in *ortho* position could also be used to give products **4n-p** in 58-64% yield.

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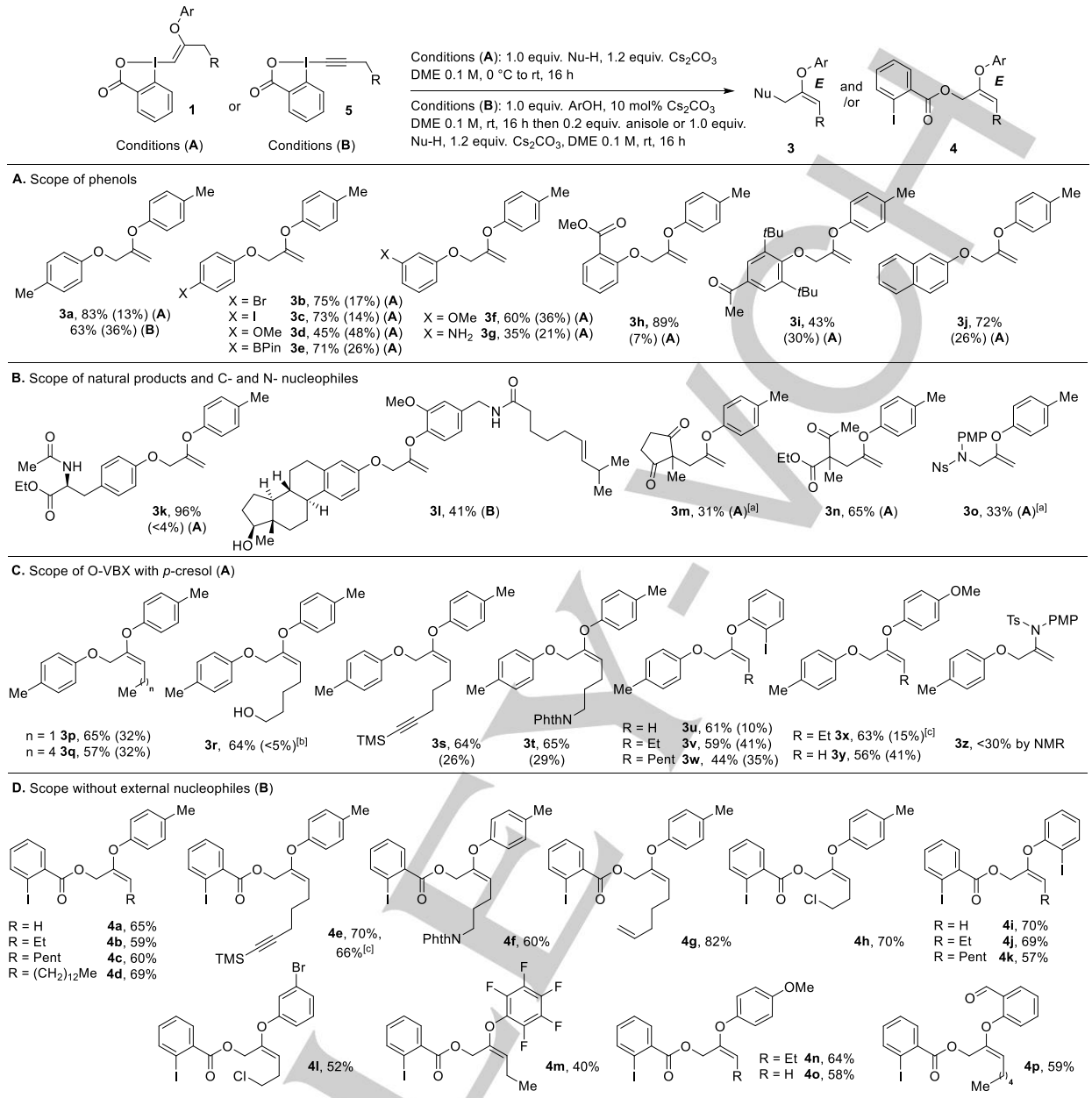

Scheme 2. Scope of the reaction. For **A. B.** and **C.** the yield of ester product **4** is given in parenthesis. [a]Only partial conversion of **1a** was observed. [b]Reaction time was 24 h. [c]The reaction was performed on gram scale.

In some cases, formation of the O-VBX reagent **1** was successful, but the reaction stopped at this stage. In particular, this was the case for secondary alkyl groups, in absence of an allylic C-H bond, for sterically hindered O-VBX or for simple VBX lacking the ether group[23] (see Scheme S1 in Supporting Information for more details). To highlight the efficiency of the transformation, gram scale syntheses were performed (Scheme 2C and 2D). Allylic ether **3x** was isolated in 63% yield using method **A**, while one-pot procedure **B** gave 66% of allylic ester **4e**. These yields are nearly identical to the one obtained on small scale, showing the robustness of the procedures.

We then examined further functionalization of the obtained aryl enol ethers (Scheme 3). The *ortho*-iodine substrate **3u** could be used in a reported palladium oxidative cyclization[24] to generate benzofuran **6** in high yield (Eq. 1). Under palladium-catalyzed hydrogenation conditions, ketone **7** resulting from cleavage of the aryl-O bond and reduction of the aryl iodide was obtained in 96% yield (Eq. 2). Finally, the electron-rich nature of the enol ether make it well-suited for oxidative modification, with the potential for accessing more highly functionalized ketones. Indeed, when using 1.2 equivalents of *meta*-chloroperbenzoic acid (*m*-CPBA) buffered with sodium bicarbonate, the epoxides **8a** and **8b** could be obtained in quantitative yield starting from the corresponding enol ethers (Eq. 3).[25] Interestingly, the addition of the *in situ* generated *meta*-chlorobenzoic acid was observed in absence of buffer to give α-benzoylated ketones such as **9a** and

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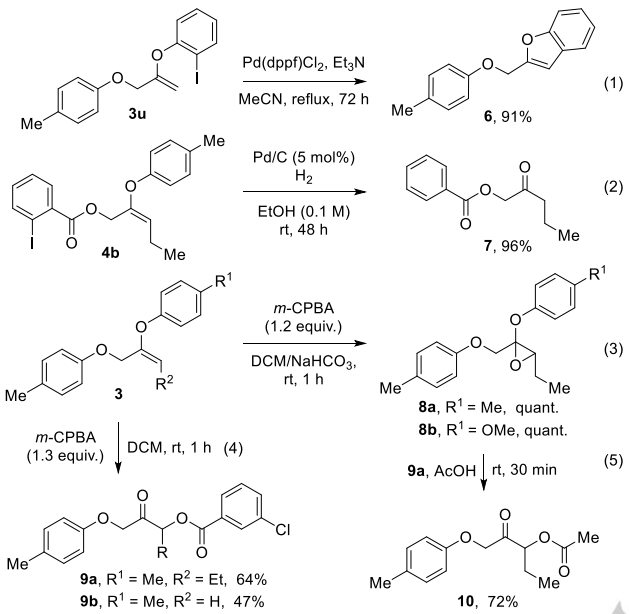
9b in moderate to good yields (Eq. 4).[26] Treatment of the isolated epoxide **8a** with acetic acid lead to the same regioselective formation of α-acetoxy ketone **10** in 72% yield (Eq. 5). This straightforward oxidation method allows to make use of the formed enol ether resulting in an overall C-H functionalization of the initial propargylic C-H bond.



Scheme 3. Product modifications.

A speculative mechanism to rationalize the observed oxy-allyl cation-like reactivity would involve the isomerization of VBX **1** to the corresponding allyl iodane under basic conditions. The high leaving group ability of hypervalent iodine[27] would then lead to the formation of an allyl cation. Indeed, ring-opening of an adjacent cyclopropane and a [4+3] reaction with furan in low yield were observed, supporting such an intermediate (See Scheme S5 and S6 in SI). However, the evidence does not allow to exclude a direct SN^2 pathway and further experiments will be needed to understand the observed transformations.

In conclusion, hypervalent iodine reagents have been used as oxy-allyl cation surrogates for the stereoselective synthesis of aryl enol ethers by reaction with phenols. In absence of external nucleophiles, the *in-situ* generated benzoate group reacted, resulting in the formation of allylic esters. The reaction most probably proceeds via an electrophilic allylic intermediate and both SN^1 or SN^2 pathways appear feasible at this stage. The obtained enol ethers could be transformed into α-difunctionalized ketones under oxidative conditions, demonstrating the synthetic utility of the transformation.

Acknowledgements

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Keywords: Hypervalent Iodine Reagents • Umpolung • Allyl Cation • Enol Ethers • Vinylbenziodoxolones

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[21] The reaction profile is usually very clean and lower yields were generally due to increase amount of ester **4a**. It is difficult to recognize clear trends in the formation of the ester products, although generally electron-rich phenols gave larger amounts of **4a**, in-line with the accelerating effect of nucleophilic additives. See Supporting Information for exact yields of isolated esters **4**.

[22] The structure of **3p** was confirmed by X-ray analysis. The data are available free of charge from the Cambridge Crystallographic Data Center (CCDC number 1989757). The structure and geometry of the other products is assumed to be the same based on the similar NMR spectra. The olefin geometry was further confirmed by NOE experiments on products **4c** and **4l**.

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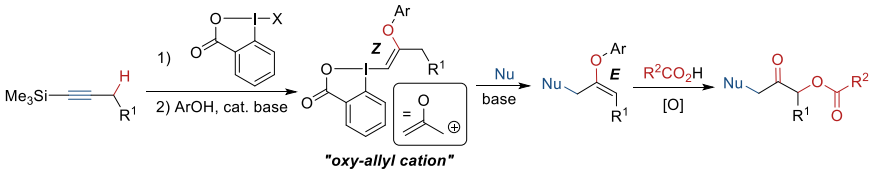

Access to oxy-allyl cation equivalents from alkynes via hypervalent iodine reagents is described. The stereoselective transformation of Vinylbenziodoxolones (VBXs) gives aryl enol ethers bearing an allylic ether or ester group and corresponds to a Umpolung of the nucleophilic reactivity of enol ethers. The obtained products are easily transformed into α-difunctionalized ketones under oxidative conditions.

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