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Stereoselective Access to Highly Substituted Vinyl Ethers via *trans*-Difunctionalization of Alkynes with Alcohols and Iodine(III) Electrophile

Wei Ding,^{†,§} Jinkui Chai,^{†,‡,§} Chen Wang,^{†,#} Junliang Wu,^{*,‡} and Naohiko Yoshikai^{*,†}

[†]Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore

^{*}College of Chemistry, Henan Institute of Advanced Technology, Zhengzhou University, Zhengzhou 450001, P.R. China [#]Zhejiang Key Laboratory of Alternative Technologies for Fine Chemical Process, Shaoxing University, Shaoxing 312000, P.R. China

Supporting Information Placeholder

ABSTRACT: A method for the regio- and stereoselective synthesis of highly substituted vinyl ethers via *trans*-1,2difunctionalization of alkynes with a cyclic λ^3 -iodane electrophile (benziodoxole triflate) and alcohols is reported. The reaction tolerates a variety of internal and terminal alkynes as well as various alcohols, affording β - λ^3 -iodanyl vinyl ethers in good yields with high regioand stereoselectivities. The benziodoxole moiety of the products can be used as a versatile linchpin for the synthesis of structurally diverse vinyl ethers that are difficult to access by other means.

Vinyl ethers are useful electron-rich olefins in organic synthesis as well as in polymer chemistry.¹ They have been utilized for valuable C-C bond forming reactions such as cycloaddition and Claisen rearrangement,² and continue to serve as workhorses for new synthetic methodology development.³ A variety of methods for the synthesis of vinyl ethers have been developed,⁴ including hydroalkoxylation of alkynes,⁵ C–O coupling between alkenyl halides or -boronates and alcohols,⁶ acid- or metal-catalyzed vinyl ether exchange,7 isomerization of allyl ethers,8 and Horner-Wittig olefination, among others (Scheme 1a).9 Nevertheless, the stereoselective synthesis of multisubstituted vinyl ethers remains a formidable challenge,¹⁰ which constitutes a major barrier for their applications with stereocontrol of tertiary and quaternary centers. The hydroalkoxylation is known for long time¹¹ and remains a subject of active research in homogeneous catalysis,¹² but is mostly limited to terminal alkynes. Alkynylbenziodoxolones have been shown to undergo stereoselective addition of phenols to afford vinyl ethers bearing a versatile benziodoxolone moiety (Scheme

1b),¹³⁻¹⁵ while this vinyl ether synthesis requires individual preparation of each iodane reagent and does not allow access to tetrasubstituted derivatives.

In contrast to the above known approaches, stereoselective addition of an alcohol to an electrophile (E^+) -activated alkyne appears to offer an attractive approach to a highly substituted vinyl ethers using a single reagent, provided that the group "E" can be used as a versatile handle for subsequent transformations. However, no such transformation has been reported for unactivated terminal and internal alkynes using common halogen electrophiles such as Br₂, I₂, and Nhalosuccinimide.¹⁶ In this respect, our attention was drawn to trivalent iodine species as potentially viable electrophiles. Thus, iodonium reagents containing triflate or fluoride have been shown to promote transdifunctionalization of alkynes with I(III) and the internal nucleophile (Scheme 1c),¹⁷⁻²⁰ while conversion of the resulting vinyl triflate into the corresponding ethers is nontrivial. Meanwhile, our group reported Zhdankin's benziodoxole triflate (BXT; 1)²¹ as an I(III) electrophile to promote "iodo(III)cyclization" of alkynes bearing nucleophilic moieties, affording heteroarenes and polycyclic arenes bearing a synthetically versatile benziodoxole group.^{22,23} Herein, we report a method to stereoselectively synthesize highly substituted vinyl ethers via trans-1,2-difunctionalization of alkynes using BXT and alcohols (Scheme 1d). The method is applicable to a variety of internal and terminal alkynes as well as various alcohols, affording the corresponding β - λ^3 -iodanyl vinyl ethers in good yields under mild and metal-free conditions. The λ^3 -iodanyl group of the products can be readily utilized for the access to structurally diverse vinyl ethers that are difficult to synthesize by existing methods.

Scheme 1. Synthetic Approaches to Vinyl Ethers

(a) Common approaches



No general approach to stereodefined tri/tetra-substituted vinyl ethers

(b) Addition to ethynylbenziodoxolone (ref 13)



(c) Alkyne trans-difunctionalization by I(III) and triflate or fluoride (ref 17, 18)

$$R^{1} = R^{2} \xrightarrow{\text{"ArlX}_{2"}} X = \text{OTf, F} \begin{bmatrix} Ar & X \\ I^{+} \\ R^{1} \xrightarrow{} \\ R^{2} \\ X \xrightarrow{} \\$$

(d) This work: Alkyne *trans*-difunctionalization by I(III) and alcohol



Using 1-phenyl-1-butyne (2a, 0.1 mmol) as a model alkyne, the desired difunctionalization proceeded smoothly using 2 equiv of 1 in MeOH (3a, 0.5 mL) at room temperature to afford the β - λ^3 -iodanyl vinyl ether 4aa in 98% yield with exclusive trans selectivity (Scheme 2a). The product 4aa could be purified by routine silica gel chromatography and proved to be stable on exposure to open air at least for one month without decomposition. The difunctionalization can also be achieved using alcohol as reagent. Thus, the reaction of 1 (2 equiv), 2a, and benzyl alcohol (3b, 5 equiv) took place in MeCN to afford the desired product 4ab in 87% yield. Et₂O could be used in place of MeCN with slightly decreased yield, while other solvents such as THF, DCE, and toluene retarded the reaction. Thus, we defined the reaction conditions using alcohol as solvent and reagent as conditions A and B, respectively. For both the conditions, the desired products could be obtained in reasonable yields (68-78%) using 1-1.2 equiv of 1 (see Tables S1–S3 for details). The addition of inorganic bases such as carbonate salts caused slight or large negative effect, while amine bases completely shut down the reaction. Note that 1 is non-hygroscopic, easy to synthesize on a decagram scale and storable at room temperature for more than a month. On the other hand, analogous reagent derived from 2-iodobenzoic

acid,²¹ which is rather hygroscopic, failed to promote the present iodo(III)etherification.

Scheme 2. Iodo(III)etherification of 1-Phenyl-1butyne (2a) with 1 and Alcohol^a



^aThe yields were determined by ¹⁹F NMR.

With the optimized reaction conditions in hand, we explored the scope of the "iodo(III)etherification" of internal alkynes (Scheme 3). A wide variety of aryl alkyl alkynes participated in the reaction with MeOH as solvent to afford the corresponding β -iodanyl vinyl ethers 4aa-4la in moderate to excellent yields with exclusive trans-selectivity. The reaction of 1-phenyl-1propyne could be performed on a gram scale (3 mmol) to afford **4ba** without compromising the yield (86%). Both electron-donating groups such as methoxy (4ea) and methyl (4fa) and electron-withdrawing groups such as ester (4ga), chloride (4ha), bromide (4ia), and trifluoromethyl (4ja) could be tolerated on the aryl group. The reaction became sluggish with 2-methyl group presumably due to the steric hindrance (see 4ka). A thienvl group could be well tolerated (see 4la). Dialkyl alkynes also proved to be amenable to the iodo(III)etherification reaction (see 4ma-4sa). Notably, unsymmetrical dialkyl alkynes bearing methyl/secondary alkyl groups or methyl/alkoxymethyl groups afforded single regioisomers as a result of methoxylation of the less hindered acetylenic carbon (see 4na-4qa). On the other hand, those bearing methyl/primary alkyl groups displayed modest regioselectivity (see 4ra and 4sa). The structures of the products 4ba and 4na were unambiguously determined by X-ray crystallographic analysis.²⁴ Note that diaryl alkynes such as diphenylacetylene did not participate in the reaction and were largely recovered.

Next, the iodo(III)etherification reactions of 2a with various alcohols were examined. The reaction of 2a with CD₃OD as reagent produced the product $4aa-d_3$ in 90% yield. A variety of primary and secondary alcohols took part in the present reaction to afford the corresponding vinyl ethers 4ab-4ao in moderate to good yields. The

reaction tolerated functional groups such as hydroxy (4ag), methoxy (4ah), cyano (4ai), bromo (4aj and 4ak), silyl (4al), allyl (4am), and carbonyl (4ao) groups on the alcohol substrate, while conditions A using alcohol as solvent gave higher yields for some functionalized alcohols (see 4ag–4ak). Naturally occurring alcohols such as (-)-menthol and androsterone were also amenable to the present iodo(III)etherification (see the products 4an and 4ao). Less nucleophilic trifluoroethanol afforded the desired product 4ap in good yield using toluene as the solvent, while tertiary alcohols such as t-BuOH failed to participate in the reaction. When the yield of the iodo(III)etherification product was low, the alkyne was typically recovered but 1 was largely decomposed to the 2-iodobenzyl alcohol derivative.

Attempts on using nucleophiles other than aliphatic alcohols, such as phenols, carboxamides, sulfonamides, and thiols, were largely futile (Figure S1), and in such cases the decomposition of **1** was observed. Nonetheless, 2-hydroxypyridine, acetic acid, and pyrazole took part in the present difunctionalization to afford the desired products **4aq–4as** in good yields.

Scheme 3. Iodo(III)etherification of Internal Alkynes^a



^{*a*}The reaction was performed on a 0.1 mmol scale. The symbol BX in the product formula refers to the benziodoxole moiety. ^{*b*}The yield for a 3 mmol-scale reaction is given in the parentheses. ^{*c*}r.r = regioisomer ratio. ^{*d*}The reaction was performed using **2a** (0.1 mmol), **1** (0.3 mmol), and allyl alcohol (**3m**; 0.3 mmol) in MeCN (0.5 mL). ^{*e*}The reaction was performed in toluene. ^{*f*}Pyrazole was used as the nucleophile.

The scope of the iodo(III)etherification reaction could be extended to terminal alkynes (Scheme 4). A variety

of aryl acetylenes reacted regio- and stereoselectively with BXT and MeOH to afford the corresponding β iodanyl vinyl ethers 6aa-6ga in moderate to high yields. The structure of **6aa** was confirmed by X-ray crystallographic analysis.²⁴ The reactions of 1-hexyne and cyclohexylacetylene also proceeded smoothly to afford the corresponding products 6ha and 6ia in good vield. Envnes such as 2-methylbut-1-en-3-vne and 1ethvnvlcvclohexene underwent chemoselective functionalization of the acetylenic moiety to furnish the 1-iodanyl-2-alkoxy-1,3-dienes 6ja and 6ka in 92% and 49% yields, respectively. In contrast to these cases, trimethylsilylacetylene underwent the iodo(III)etherification with opposite regioselectivity to afford the β -silvl vinyl ether **6la** in 81% yield, presumably due to the ability of the silvl group to stabilize positive charge at the β -position.^{17a,24} Like the reactions of internal alkynes, a variety of primary and secondary alcohols took part in the reaction with phenylacetylene to afford the products 6ab-6at in moderate to high yields.

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Scheme 4. Iodo(III)etherification of Terminal Alkynes^a



^{*a*}The reaction was performed on a 0.1 mmol scale. The symbol BX in the product formula refers to the benziodoxole moiety. ^{*b*}The reaction was performed with **5a** (0.1 mmol), BXT (0.3 mmol), and allyl alcohol (0.3 mmol), and MeCN (0.5 mL).

The present iodo(III)etherification is considered to involve electrophilic activation of the alkyne by a BX cation upon dissociation of triflate from BXT.¹⁵ This would trigger nucleophilic addition of the alcohol to the C=C bond in a *trans*-fashion with Markovnikov-type regioselectivity, eventually affording the β -iodanyl vinyl ether along with HOTf. DFT calculations supported this mechanistic picture, and also reproduced the regioselectivity trend observed for 4-methylpent-2-yne and hex-2-yne (see 4na/4sa and Figures S8-S10). studies reaction Kinetic on the of 4trifluoromethylphenylacetylene (**5b**) in MeOH, using ¹⁹F NMR, revealed first-order dependence on both 1 and 5b (Figures S6 and S7), in support of rate-limiting transiodo(III)etherification. It is notable that the vinyl ether product remains intact in the presence of strongly acidic HOTf, presumably due to steric and electronic protection by the bulky and electron-withdrawing iodanyl group.

The β -iodanylyinyl ethers obtained by the present method serve as versatile starting materials for the stereoselective synthesis of highly substituted vinyl ethers. As illustrated in Scheme 5a, the product 4ba smoothly underwent Pd-catalyzed Stille, Sonogashira, and Suzuki–Miyaura coupling to afford conjugated vinyl ethers 7, 8, and 9, respectively, in good yields with retention of the stereochemistry.14c-e In addition, Rosenmund-von Braun cyanation²⁵ and reduction of the benziodoxole moiety in 4ba could be selectively achieved at different temperatures. Thus, B-cvano and iodo vinyl ethers 10 and 11 were obtained in good yields at 90 °C and 50 °C, respectively. The Pd-catalyzed hydrodehalogenation of the BX moiety in 4ba also proceed smoothly, and the product then took part in ytterbium triflate-catalyzed Mannich reaction,²⁶ inverse electron-demand hetero-Diels-Alder reaction with in situ generated 1,2-diaza-1,3-diene,27 and cyclopropanation with dichlorocarbene, affording βamino ketone 12, tetrahydropyridazine 13, and cyclopropane 14, respectively, in moderate yields over two steps (Scheme 5b). Furthermore, β -iodanylvinyl allyl ethers 4am and 6am underwent Cu-promoted reduction and Claisen rearrangement to afford a-iodo homoallyl ketones 16a and 16b, respectively, in good vields (Scheme 5c).

Scheme 5. Product Transformations

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In summary, we have developed a regio- and stereoselective trans-1,2-difunctionalization reaction of alkynes with a cyclic λ^3 -iodane electrophile and alcohols as a versatile approach to highly substituted vinyl ethers. The present iodo(III)etherification proceeds under simple and mild conditions and tolerates various internal and terminal alkynes as well as a broad range of alcohols, affording air- and moisture-stable trans-Biodanylvinyl ethers. The benziodoxole moiety of the products can be utilized as a synthetic linchpin in various transformations, allowing for stereocontrolled preparation of multisubstituted vinyl ethers. We anticipate that previously unimaginable stereodefined vinyl ethers, which are made accessible by the present method, will not only enhance the scope and the utility of existing vinyl ether transformations but also inspire the development of their new synthetic transformations. Further studies on the use of benziodoxole triflate and related compounds as electrophilic λ^3 -iodanation agents are also ongoing in our laboratory.

ASSOCIATED CONTENT

Experimental procedures and characterization data for all the new products (PDF).

Crystallographic data for **4ba** (CIF)

Crystallographic data for 4na (CIF)

Crystallographic data for 6aa (CIF)

Crystallographic data for 6la (CIF)

AUTHOR INFORMATION

Corresponding Author

*wujl@zzu.edu.cn *nyoshikai@ntu.edu.sg

Author Contributions

§These authors contributed equally.

Notes

The authors declare no competing financial interests.

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