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

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ABSTRACT: A method for the regio- and stereoselective synthesis of highly substituted vinyl ethers via *trans*-1,2-difunctionalization 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 regio- and 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. Hydroalkoxylation has been known for a 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 ether using a single reagent, provided that the group “E” can be used as a versatile handle for subsequent *trans*-formations. However, no such transformation has been reported for unactivated terminal and internal alkynes using common halogen electrophiles such as Br_2 , I_2 , and N-halosuccinimide.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 *trans*-difunctionalization 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.

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. Et_2O 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, 76

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Scheme 1. Synthetic Approaches to Vinyl Ethers

(a) Common approaches

Problem:

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) (d) This work: Alkyne *trans*-difunctionalization by I(III) and alcohol Scheme 2. Iodo(III)etherification of 1-Phenyl-1-butyne (2a) with 1 and Alcohol^a

(a)

(b)

^aThe yields were determined by ¹⁹F NMR.

reaction. Note that **1** is nonhygroscopic, easy to synthesize on a decagram scale, and storable at room temperature for more than a month. On the other hand, an analogous reagent derived from 2-iodobenzoic acid,²¹ which is rather hygroscopic, failed to promote the present iodo(III)etherification.

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-1-propyne 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 the 2-methyl group presumably due to the steric hindrance (see **4ka**). A thienyl 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 moderate 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-d₃** 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 to use 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.

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

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 a slight or large negative effect, while amine bases completely shut down the

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

^aThe reaction was performed on a 0.1 mmol scale. The symbol BX in the product formula refers to the benziodoxole moiety. ^bThe yield for a 3-mmol-scale reaction is given in the parentheses. ^cr.r. = regioisomer ratio. ^dThe reaction was performed using 2a (0.1 mmol), 1 (0.3 mmol), and allyl alcohol (3m; 0.3 mmol) in MeCN (0.5 mL). ^eThe reaction was performed in toluene. ^fPyrazole was used as the nucleophile.

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

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

yield. Enynes such as 2-methylbut-1-en-3-yne and 1-ethynylcyclohexene 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 -silyl vinyl ether **6la** in 81% yield, presumably due to the ability of the silyl 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.

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 $\equiv$ 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). Kinetic studies on the reaction of 4-trifluoromethylphenyl-

145 of 1-hexyne and cyclohexylacetylene also proceeded smoothly
146 to afford the corresponding products **6ha** and **6ia** in good

acetylene (**5b**) in MeOH, using ^{19}F NMR, revealed first-order dependence on both **1** and **5b** (Figures S6 and S7), in support of rate-limiting *trans*-iodo(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 -iodanylvinyl 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

moderate yields over two steps (Scheme 5b). Furthermore, β -iodanylvinyl allyl ethers **4am** and **6am** underwent Cu-promoted reduction and Claisen rearrangement to afford α -iodo homoallyl ketones **16a** and **16b**, respectively, in good yields (Scheme 5c).

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*- β -iodanylvinyl 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 -iodination agents are also ongoing in our laboratory.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.0c04140>.

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)

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Scheme 5. Product Transformations

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, β -cyano and -iodo vinyl ethers **10** and **11** were obtained in good yields at 90 and 50 °C, respectively. The Pd-catalyzed hydrodehalogenation of the BX moiety in **4ba** also proceed smoothly, and the product then took part in a 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 β -amino ketone **12**, tetrahydropyridazine **13**, and cyclopropane **14**, respectively, in

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254 Author Contributions

255 [†]W.D. and J.C. contributed equally.

256 Notes

257 The authors declare no competing financial interest.

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