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Title:

Regio-, and stereoselective iodobromination of ynamides for synthesis of (*E*)-1-bromo-2-iodoenamides

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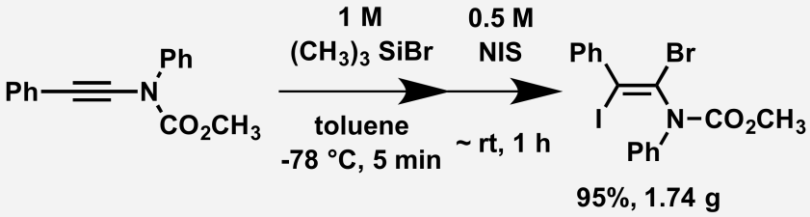
Abstract: (Your abstract must use **Normal style** and must fit in this box. Your abstract should be no longer than 300 words. The box will 'expand' over 2 pages as you add text/diagrams into it.)

Enamides are valuable intermediates in organic synthesis, because of their ability to serve as building blocks in a wide variety of functional group transformations. They have also been found as a substructure in natural products and pharmaceuticals. Moreover, they recently have emerged as a novel type of nucleophiles in stereoselective C-C bond-forming reactions. From the synthetic point of view, vicinal dihaloenamides are versatile variants of enamides. The reactive bonds between sp^2 carbon and halogen are advantageous to chemical transformation, and this beneficial point would expand the possibilities and importance of enamide structure. The bromoiodoenamides are especially useful, as they could be converted into functional groups by way of transition metal-catalyzed reactions and halogen-metal exchange. Despite the utility of vicinal dihaloalkenes, their synthetic availability still remains a challenge due to the inherent difficulty in regio-, and stereoselective iodobromination of alkynes. The stoichiometric addition of iodobromine (IBr) is one way to prepare the dihaloalkene; however the hygroscopic and hazardous IBr is inconvenient, and this often results in isomeric mixtures.

Herein we report the first example of a synthesis of the vicinal bromoiodoenamides: commercially available IBr and/or *in situ* generated IBr formed ynamides into single isomer of (*E*)-1-bromo-2-iodoenamides (Scheme 1). The *in situ* IBr was successfully generated from bromotrimethylsilane (TMSBr) and *N*-iodosuccinimide (NIS), and the IBr exactly added in *anti*-mode to ynamides according to the nature of the keteniminium resonance form. In the case that the commercial IBr didn't work well, the *in situ* IBr proved to be an alternatively prosperous reagent. Thus, the method provides a straightforward access to general entry of (*E*)-1-bromo-2-iodoenamides.



Scheme 1. Regio-, and stereoselective iodobromination of ynamides to (*E*)-1-bromo-2-iodoenamides.