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Title:

Synthesis of 1-haloethenamides from ynamides through halotrimethylsilane-mediated hydrohalogenation

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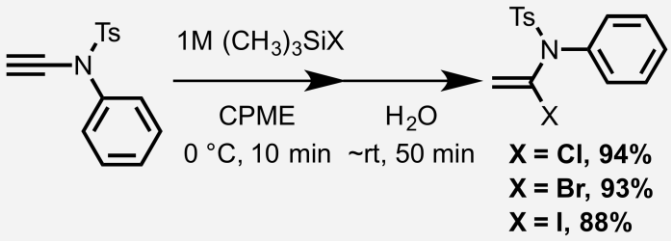
Abstract: (Your abstract must use **Normal style** and must fit in this box. Your abstract should be no longer than 300 words. The box will 'expand' over 2 pages as you add text/diagrams into it.)

Vinyl halides are clearly important structure in organic synthesis, because of their ability to serve as building blocks in a wide variety of chemical transformations. The weakly bonded halogens are highly reactive and incredibly useful toward construction of complex molecules. From the synthetic point of view, haloenamides are versatile variants of vinyl halides. Haloenamides in *exo*-methylene fashion, namely 1-haloethenamide, is especially instructive: the sterically unhindered moiety and *N*-substituted halovinyl is potentially effective for synthesizing nitrogen-containing compounds. Despite the intriguing utility of 1-haloethenamide, their synthetic availability still remains a challenge, because of the inherent difficulty in hydrohalogenation. The stoichiometric addition of hydrogen halide (HX) to terminal alkyne of ynamide is one way to prepare 1-haloethenamide; however, the generation and transfer of hygroscopic and gaseous HX are inconvenient to perform, and the problem associated with this type of reactions lies in the formation of isomeric mixtures and side-products. Although an alternative hydrometallation exists, it requires several reaction steps and extra operations.

Herein we report the first example of a synthesis of 1-haloethenamides from ynamides using *in situ* generated HX from 1 M halotrimethylsilane (TMSX; X = Cl, Br, I) and 20 equiv of H_2O (Scheme 1). The HX was cleanly added to terminal alkyne of ynamide within 1 h, giving desired 1-haloethenamides in high yields. The deuteriobromination experiments revealed this addition reaction proceeds with regio- and stereoselective manner in *anti*-mode. In addition, the resultant products were applicable to transition metal-catalysed reaction. Thus, the protocol provides simple access to 1-haloethenamide substructures.



Scheme 1. Synthesis of 1-haloethenamides from ynamides through *in situ* generated HX