(4) Organic:

2643 - Regio- and stereoselective synthesis of (*E*)-1-bromo-2-iodoalkenes from internal alkynes

View Session Detail

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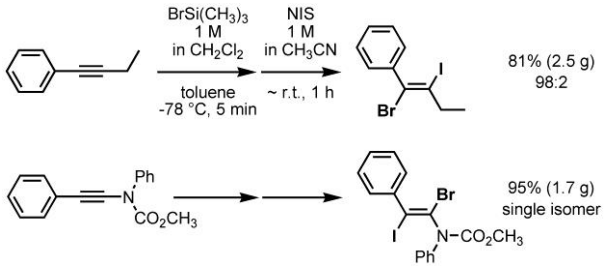
Abstract Body: Tetrasubstituted olefins bearing four different carbon-linked groups have played an important role in organic chemistry, because of their ability to serve as bioactive molecules, and potentially therapeutics. They also have been found as substructure in organic material sciences. In addition, the olefins have been employed as key building blocks for producing adjacent chiral-carbon centers through face-selective addition reactions. Despite of the utility of the alkenes, their synthetic availability remains a challenge owing to difficulty in geometrically defined olefin synthesis. The endocyclic versions having distinct geometry are somewhat achievable by way of several protocols (e.g. carbonyl olefination, olefin metathesis, and cycloaddition); however, for the single formation of acyclic version, those protocols encounter problem of low stereo-chemical control. Even though the carbometallation, a most widely used for preparation of poly-substituted alkenes, requires a directing group to control the stereo-selectivity, which has limited utilities for unsymmetrically internal alkyne substrates. This drawback causes poor generality concerning substrate tolerance, metal option, and a diversity of products on the reaction.
Herein we present a synthesis of vicinal bromoiodoalkenes from internal alkynes in a highly regio- and stereo-selective manner (Scheme 1). The key reagent was *in situ* IBr that was prepared from bromotrimethylsilane (TMSBr) and *N*-iodosuccinimide (NIS). The IBr underwent the addition reaction to conventional aliphatic alkynes having no heteroatoms for control, although commercially available IBr didn't work well. The method was also readily amenable to ynamides, giving corresponding enamides.



Scheme 1. Regio-, and stereoselective iodobromination of alkynes.