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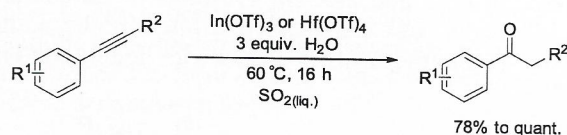
ALKYNE HYDRATION AND HYDROHALOGENATION IN LIQUID SULFUR DIOXIDE

Krista Suta

Faculty of Materials Science and Applied Chemistry, Riga Technical University,
P. Valdena 3/7, Riga, LV-1048, Latvia
e-mail: krista.suta@gmail.com

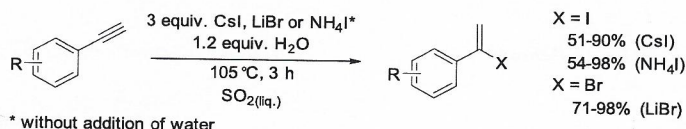
Sulfur dioxide is not only a useful building block in a synthetic organic chemistry but in its liquid state ($\text{SO}_{2(\text{liq.})}$) can be used as a strong polar solvent as well [1-3]. Herein we report a catalytic alkyne hydration and a new approach for the alkyne hydrohalogenation promoted by $\text{SO}_{2(\text{liq.})}$ as a reaction medium.

Hydration of alkynes is useful reaction for introduction of valuable carbonyl functionality. Nowadays, instead of the use of environmentally hazardous mercury salts, the main strategy for the alkyne hydration is the use of transition metal catalytic systems and acidic solvents or additives. Combination of In (III) or Hf (IV) triflate as a catalyst and $\text{SO}_{2(\text{liq.})}$ as a solvent allowed us to obtain desired arylketones in good to excellent yields without direct addition of acid (Scheme 1). Due to the medium effects the catalyst loadings can be reduced to less than 1 mol% for electron rich alkynes without loss in yields.



Scheme 1 Alkyne hydration in $\text{SO}_{2(\text{liq.})}$

Hydrohalogenation of alkynes is a straightforward strategy for synthesis of vinyl halides. Screening of ammonium and group 1 and 2 halides for reactivity towards phenylacetylene in $\text{SO}_{2(\text{liq.})}$ revealed that CsI, LiBr and NH_4I provided up to almost quantitative conversion of starting material into the desired vinyl halide. After optimization of the reaction conditions a series of aryl vinyl iodides and bromides were synthesized with moderate to excellent yields (Scheme 2).



Scheme 2 Alkyne hydrohalogenation in $\text{SO}_{2(\text{liq.})}$

Supervisor: Prof. Māris Turks

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