



10TH PAUL WALDEN SYMPOSIUM ON ORGANIC CHEMISTRY

Programm and Abstracts

Riga
June 15-16, 2017

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Alkyne Transformations in Liquid SO₂

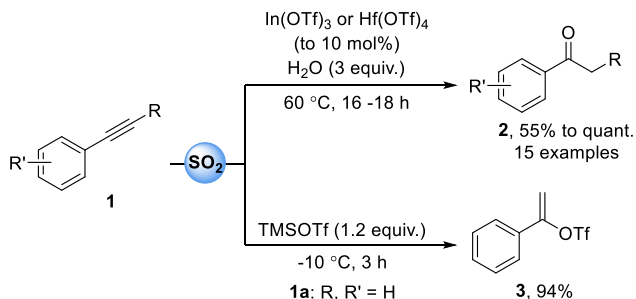
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Sulfur dioxide (SO₂) is not only a useful building block in a synthetic organic chemistry but in its liquid state (SO₂(liq.)) can be used as a strong polar solvent as well [1-3]. Herein we report a catalytic alkyne hydration and a new approach for the alkyne hydrohalogenation promoted by SO₂(liq.) as a reaction medium.

Hydration of alkynes is one of the most direct approach for introduction of carbonyl functionality in organic molecules. 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 SO₂(liq.) as a solvent allowed us to obtain desired arylketones **2** in good to excellent yields without direct addition of acid (Scheme 1). Therefore, for electron rich alkynes catalyst loadings can be reduced to less than 1 mol% without loss in yields. Hydration of aliphatic or strong electron accepting group containing arylalkynes was not successful so far.

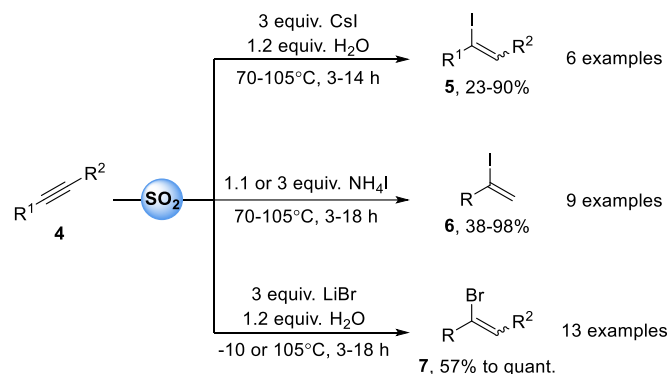
In some cases, corresponding vinyl triflate was detected as a side product in a reaction mixture of alkyne hydration. Further, when phenylacetylene (**1a**) was allowed to react with TMSOTf in SO₂(liq.) at -10 °C (reflux) full conversion of starting material to vinyl triflate **3** was reached in 3 h.



Scheme 1. Alkyne hydration and vinyl triflate synthesis in liquid SO₂.

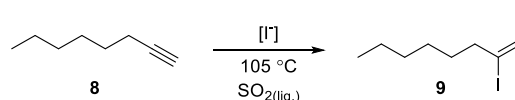
Hydrohalogenation of alkynes is one of the most straightforward strategies for synthesis of vinyl halides. Screening of different alkali, alkaline earth metals and ammonium halides (I, Br, Cl, F) for reactivity towards phenylacetylene in liquid SO₂

showed potential of CsI, LiBr and NH₄I as halide sources reaching up to almost quantitative conversion of starting material to desired α -vinyl halide detected by GC. Furthermore, NH₄I works as iodide as well as proton source in the reaction medium. After optimization of the reaction conditions a series of α -aryl vinyl iodides **5** and **6** and bromides **7** were synthesized in moderate to excellent yields (Scheme 2).



Scheme 2. Alkyne hydrohalogenation in liquid SO₂.

While LiBr did not react with aliphatic alkynes under the optimized reaction conditions for hydrohalogenation, CsI and NH₄I led to the mixture of unreacted starting material and 1,2-diiodide (Scheme 3). Phenylacetylenes substituted with electron accepting groups also led to the formation of 1,2-diiodide without α -vinyl iodide detected.



Scheme 3. Reactivity of 1-octyne (**8**) towards iodide in liquid SO₂.

Supervisor: Dr. chem. M. Turks

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