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ON ORGANIC CHEMISTRY**

**Programm and Abstracts**

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|   |    |
|---|----|
| <b>Rimants Zogota, Linda Kinena.</b> The development of aspartic-protease inhibitors for malaria treatment .....  | 37 |
| <b>Elīna Zoltnere, Uldis Peipiņš.</b> The 1 <sup>st</sup> generation dendrimeric antioxidants of arylmethyl Meldrum's acids .....                               | 38 |
| <b>Dace Cīrule.</b> Nucleoside silylation and reactions of triazolypurine derivatives with nucleophiles ...   | 39 |
| <b>Diana Dzabijeva.</b> The studies on the antiradical activity kinetics of the different antibacterial plant extracts.....                                     | 40 |
| <b>Livia Matt.</b> Hydroformylation of olefinic derivatives of isosorbide and isomannide.....   | 41 |
| <b>Kristers Ozols.</b> 2/6-Azido-6/2-alkylthiopurine synthesis and DFT study .....  | 42 |
| <b>Armands Ruduss.</b> Synthesis and properties of 3-(diphenylamino)carbazole moiety containing chromophores for organic solar cell application .....           | 43 |
| <b>Armands Sebris, Zigfrīds Kapilinskis.</b> Synthesis of fluorescent purine derivatives with N(9) amorphousing groups .....                                    | 44 |
| <b>Marcis Sejejs, Artis Kinens.</b> Tetrazole hemiaminal as a chiral auxiliary .....  | 45 |
| <b>Anda Sīpola.</b> Diastereodivergent synthesis of amino epoxides .....  | 46 |
| <b>Krista Suta.</b> Alkyne transformations in liquid SO <sub>2</sub> .....  | 47 |
| <b>Sindija Zēberga.</b> Practical synthetic approach towards lepadins.....  | 48 |
| <b>Konstantinos Grammatoglou, Jekaterina Sirotkina.</b> C-Quaternary alkynyl glycinols <i>via</i> the Ritter reaction of cobalt complexed alkynyl glycols ..... | 49 |
| <b>Toms Kalnins.</b> Abstract withdrawn.....  | 50 |
| <b>Artis Kinēns, Simonas Balkaitis.</b> Synthesis of chiral DMAP catalysts.....   | 51 |
| <b>Ilze Kumpiņa.</b> Iron catalysed synthesis of arylphosphonic acid esters.....  | 52 |
| <b>Anna Lielpētere.</b> Electrochemical generation of carbenium ions <i>via</i> electroauxiliary.....   | 53 |
| <b>Ruslan Muhamadejev.</b> Intramolecular hydrogen bonds in 1,4-dihydropyridine derivatives .....   | 54 |
| <b>Anete Parkova.</b> Cyclic boronic acids as beta-lactamase inhibitors .....   | 55 |
| <b>Elina Petrova.</b> Synthesis of peptidic $\alpha$ -ketoamide analogues of known PfSUB1 inhibitor.....  | 56 |
| <b>Aleksandrs Pustenko.</b> Carbonic anhydrases: inhibitor synthesis .....  | 57 |
| <b>Marija Skvorcova.</b> Intramolecular cyclopropylmethylation <i>via</i> non-classical carbenium ion.....  | 58 |
| <b>Diāna Zača.</b> Synthesis of potential epigenetic enzyme inhibitors.....   | 59 |
| <b>Diāna Zeļencova.</b> Mapping of the active site of $\epsilon$ -trimethyllysine hydroxylase.....  | 60 |

# Alkyne Transformations in Liquid SO<sub>2</sub>

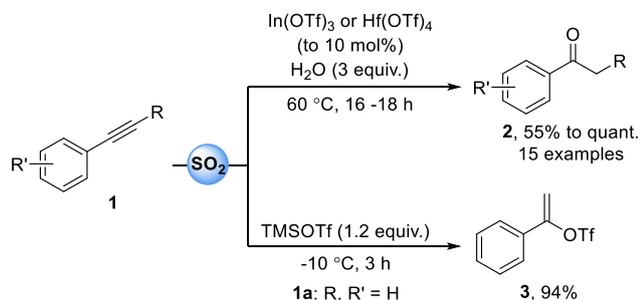
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Sulfur dioxide (SO<sub>2</sub>) is not only a useful building block in a synthetic organic chemistry but in its liquid state (SO<sub>2(liq.)</sub>) can be used as a strong polar solvent as well [1-3]. Herein we report a catalytic alkyne hydration and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

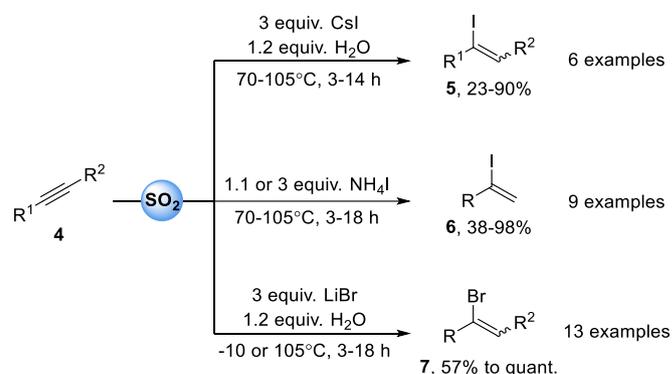
In some cases, corresponding vinyl triflate was detected as a side product in a reaction mixture of alkyne hydration. Further, when phenylacetylene (**1a**) was allowed to react with TMSOTf in SO<sub>2(liq.)</sub> at -10 °C (reflux) full conversion of starting material to vinyl triflate **3** was reached in 3 h.



**Scheme 1.** Alkyne hydration and vinyl triflate synthesis in liquid SO<sub>2</sub>.

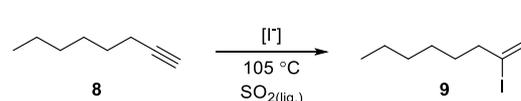
Hydrohalogenation of alkynes is one of the most straightforward strategies for synthesis of vinyl halides. Screening of different alkali, alkaline earth metals and ammonium halides (I, Br, Cl, F) for reactivity towards phenylacetylene in liquid SO<sub>2</sub>

showed potential of CsI, LiBr and NH<sub>4</sub>I as halide sources reaching up to almost quantitative conversion of starting material to desired  $\alpha$ -vinyl halide detected by GC. Furthermore, NH<sub>4</sub>I works as iodide as well as proton source in the reaction medium. After optimization of the reaction conditions a series of  $\alpha$ -aryl vinyl iodides **5** and **6** and bromides **7** were synthesized in moderate to excellent yields (Scheme 2).



**Scheme 2.** Alkyne hydrohalogenation in liquid SO<sub>2</sub>.

While LiBr did not react with aliphatic alkynes under the optimized reaction conditions for hydrohalogenation, CsI and NH<sub>4</sub>I 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  $\alpha$ -vinyl iodide detected.



**Scheme 3.** Reactivity of 1-octyne (**8**) towards iodide in liquid SO<sub>2</sub>.

Supervisor: Dr. chem. M. Turks

## REFERENCES

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