77.

Latvijas Universitātes starptautiskā zinātniskā konference

ĶĪMIJAS SEKCIJA

2019. gada 8. februāris

Tēžu krājums

LATVIJAS UNIVERSITĀTE
ANNO 1919

77.

Latvijas Universitātes starptautiskā zinātniskā konference

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CATIONIC REARRANGEMENT REACTIONS OF PROPARGYL SILANES

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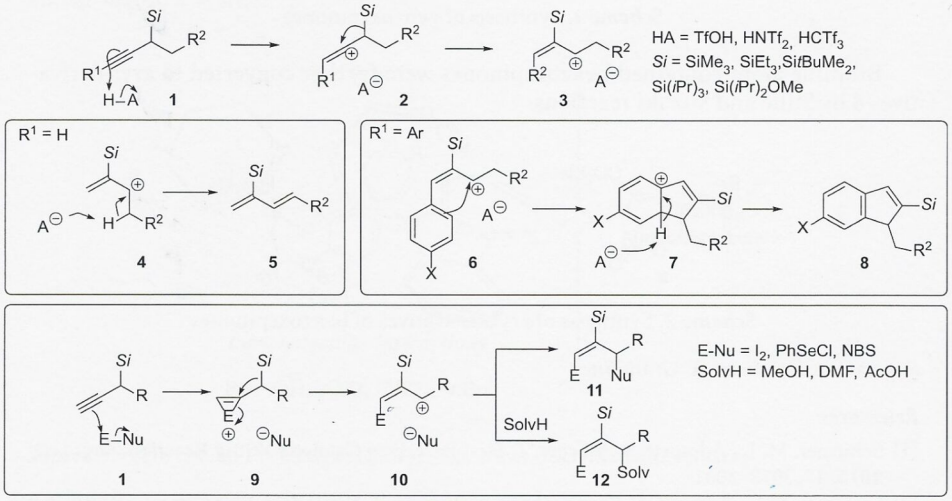
Hosomi-Sakurai type reactivity of propargyl silanes towards electrophiles has been well documented. In some cases, 1,2-silyl shift in the intermediate β-silyl vinyl carbenium ion has been observed [1]. Here we report the generation of allyl carbenium ions from propargyl silanes by electrophilic activation. Three reactivity pathways are operational. Deprotonation to give silyl dienes, intramolecular cyclisation to give silyl indenes and intermolecular addition to give allyl functionalized vinyl silanes.

Protonation of the triple bond of propargyl silanes with strong Brønsted acids results in formation of allyl carbenium ions **3** (Scheme 1). If R^1 = H, deprotonation gives silyl dienes **5**. In aryl substituted carbenium ions **6** both deprotonation and intramolecular attack to give silyl indenes **8** can occur. Selectivity is influenced by polarity of the solvent, electronic properties of aryl substituents and the Brønsted acid used.

Activation of the triple bond with electrophilic halogen reagents results in allyl carbenium ions **10**. Addition of the conjugate nucleophile gives allyl functionalized vinyl silanes **11**. If a nucleophilic solvent is used, formation of vinyl silanes **12** is observed.



Scheme 1. Electrophilic activation of propargyl silanes.

Supervisor: prof., Dr. chem. M. Turks

References:

[1] Danheiser, R. L., Dixon, B. R., Gleason, R. W. *J. Org. Chem.* **1992**, *57*(23), 6094–6097.

SYNTHESIS AN OF FUNCTIONA CONJUGATES

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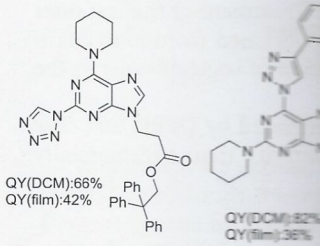
Earlier we reported the and the synthesis of 2/6-tr position. Different electron the purine structure that increased amorphous prop capabilities [3].

In this work, the synth amine electron-donor grou Purine *N*(9) position was moieties. The fluorescent Quantum yields in DCM



Acknowledgements: *This work kovskis and Dr. A. Vembris a lations.*

Supervisor: Dr. chem. M. Turk

References:

[1] Kovaļovs, A., Novosjolova, Turks, M. *Tetrahedron Lett.*
[2] Traskovskis, K., Mihailovs, *8434*: Nonlinear Optics and
[3] Puckyte, G., Schmaltz, B., Bouclé, J., Tran-Van, F. *J. P*