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27th CROATIAN MEETING OF CHEMISTS AND CHEMICAL ENGINEERS

WITH INTERNATIONAL PARTICIPATION • 5th SYMPOSIUM "VLADIMIR PRELOG"
5-8 OCTOBER 2021 • VELI LOŠINJ, HOTEL PUNTA, CROATIA

BOOK OF ABSTRACTS



27th CROATIAN MEETING OF CHEMISTS AND CHEMICAL ENGINEERS
27. HRVATSKI SKUP KEMIČARA I KEMIJSKIH INŽENJERA
5–8 October 2021, Veli Lošinj, Croatia

27th Croatian Meeting of Chemists and Chemical Engineers

with international participation

5th Symposium Vladimir Prelog

5 – 8 October 2021

Veli Lošinj, Vitality Hotel Punta, Croatia

BOOK OF ABSTRACTS

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EXPLORATION OF VARIOUS ELECTROPHILE-INDUCED TRANSFORMATIONS OF PROPARGYL SILANES

Rūdolfs Belaunieks, Mikus Puriņš, Viktors Kumpiņš, Māris Turks*

Institute of Technology or Organic Chemistry, Faculty of Materials Science and Applied Chemistry, Riga Technical University, P. Valdena str. 3, Riga, LV-1048

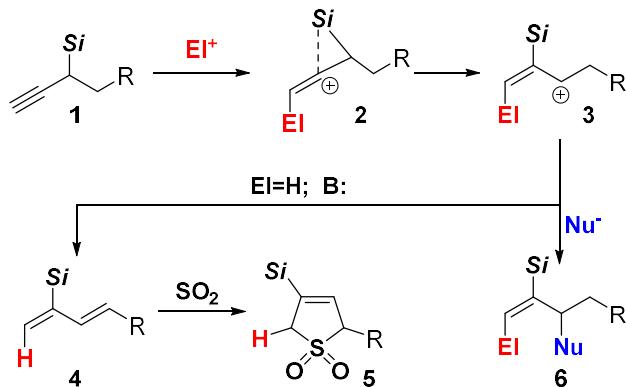
* Maris.Turks@rtu.lv

Stabilizing properties of silicon in reactions, that proceeds via β -silyl carbenium ion, is commonly known as β -silicon effect. Mechanistic insights show two possible pathways of stabilization – vertical (e.g. hyperconjugation) or non-vertical (e.g. silonium ion).^[1] Formation of closed silonium ion with combination of other stabilizing effects explains why many reactions involving β -silyl carbenium ion tend to undergo 1,2-silyl shift.

Previously we have reported the use of propargylsilanes **1** in the synthesis of silyl dienes and indenes by the catalytic amounts of strong Brønsted acids (TfOH , Tf_2NH , Tf_3CH) that involves 1,2-silyl shift.^[2]

Herein, we report the use of liquid sulfur dioxide for this transformation as a highly polar and Lewis acidic reaction media, which offers possibility to use weaker acids (e.g. BzOH , TsOH). Moreover, in a tandem cheletropic addition process silyl sulfolenes **5** are obtained from the *in situ* formed dienes **4**.^[3]

To expand this concept further, other electrophiles have been used to activate propargyl silane moiety to obtain intermediate **3**. The latter can react with various nucleophiles to obtain compounds **6**.



Scheme 1. Electrophile induced transformations of propargyl silanes

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