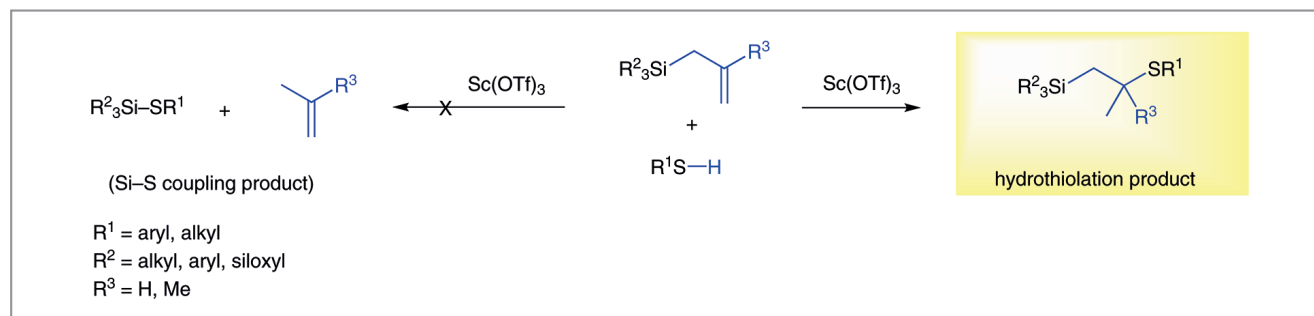


Highly Selective Hydrothiolation of Unsaturated Organosilicon Compounds Catalyzed by Scandium(III) Triflate

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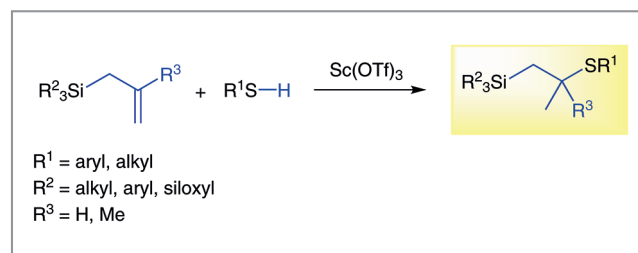
Scheme 1

Many research groups around the world have been looking for efficient synthetic methods which would allow introduction of the thioether functionality into unsaturated systems. The hydrothiolation reaction, known also as the thiol-ene or thiol-yne coupling, has attracted significant attention because of its simplicity and practical use in various fields of chemistry and materials science. Moreover, the reaction conditions are very mild in the majority of reports.

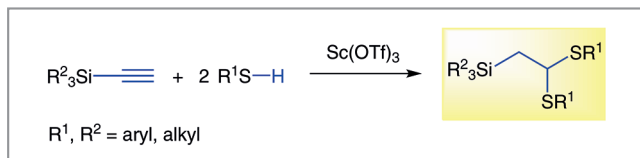
For many years, the main area of concern at the Department of Organometallic Chemistry, Adam Mickiewicz University in Poznań has been broadly defined as organosilicon chemistry. Recently, the research work of Dr. Grzegorz Hreczycho's group has also been directed towards novel applications of unsaturated organosilicon compounds in reactions catalyzed by Lewis acids. As Dr. Hreczycho put it: "After the successful O-silylation of silanols and silanediols by alkenylsilanes, we decided to extend our work on the O-H bond to other groups with similar properties, like S-H." Surprisingly, the formation of an Si-S bond was not observed. Instead of Si-S coupling, the selective hydrothiolation of allylsilanes was observed (Scheme 1). Professor Marciniec, one of the authors of this work, commented: "A lot of scientists would have moved on, but our group always faces the problems. We therefore decided to exploit this unpredicted activity to achieve novel applications of the hydrothiolation of organosilicon compounds."

"To the best of our knowledge, all earlier research on the addition of thiols to allylsilanes has been based on free-radical reactions. In these, the substrates are activated by temperature, UV radiation or free-radical generators and as far as we

know, no catalytic method of allylsilane hydrothiolation has yet been reported," said Dr. Hreczycho. "The graduate student Krzysztof Kuciński – who is working towards his doctorate under the supervision of Dr. Piotr Pawluć – started with tests of various catalysts and solvents. Scandium(III), bismuth(III), indium(III) and samarium(III) triflates were considered as catalyst for this process," he continued. "Among the above-mentioned triflates, only scandium(III) triflate and indium(III) triflate were found to be active catalysts, although scandium(III) triflate demonstrated the highest activity and selectivity in the hydrothiolation reaction. Toluene and fluorobenzene proved to be the most suitable solvents for this process." Subsequently, the nature of substituents attached to silicon and sulfur was examined and proved to be insignificant for the reaction. The use of allylsilanes in hydrothiolation catalyzed by scandium(III) triflate led to the products consistent with Markovnikov's rule (Scheme 2). This result was confirmed by ^1H NMR spectroscopy.



Scheme 2



Scheme 3

“The radical type of hydrothiolation leads to the anti-Markovnikov regioisomer. Our discovery not only reports an unprecedented use of Lewis acids in allylsilane hydrothiolation, but it is also the first reaction to allow access to Markovnikov regioisomers in this kind of process,” said Dr. Hreczycho, adding: “Therefore, each product obtained by us in these reactions was classified as a novel thioether-functionalized silane. The curiosity and enthusiasm of Krzysztof Kuciński, who performed the experiments, made us go further and investigate ethynylsilanes as well.” These compounds showed relatively high reactivity in the hydrothiolation catalyzed by scandium(III) triflate; however, the reaction was slower (Scheme 3). Indium(III) triflate proved to be inactive in this process. As a result, the Poznań based researchers obtained various products of double-addition.

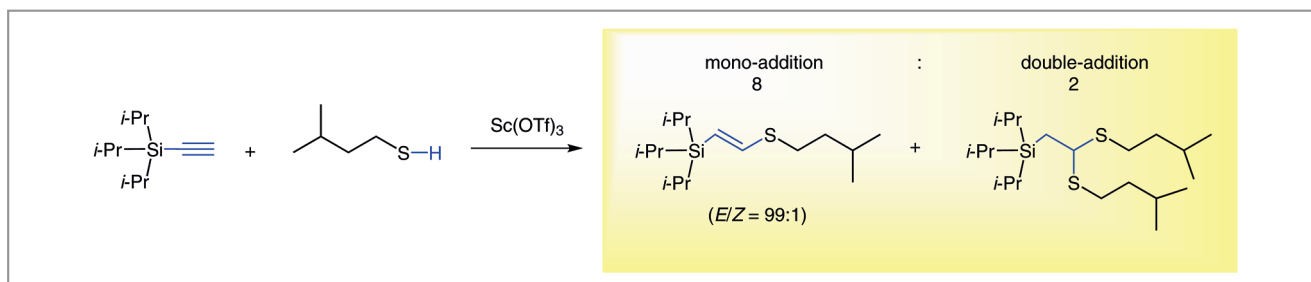
Dr. Piotr Pawluć suggested the possibility of obtaining a mono-addition product by the use of equimolar amounts of substrates. Indeed, when the reaction of ethynyltriisopropylsilane with 3-methylbutanethiol in a 1:1 ratio was performed, the mono-addition product was predominantly obtained

in the anti-Markovnikov fashion ($E/Z = 99:1$). However, the mono-addition product was still contaminated by double-addition product (Scheme 4).

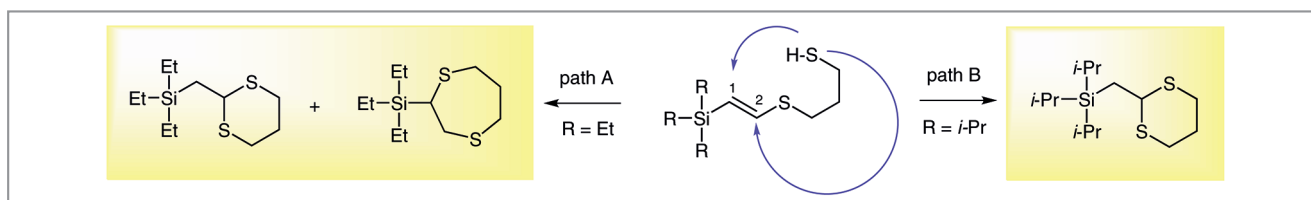
A very interesting example was the reaction between ethynyltriethyl- and ethynyltriisopropylsilane with propane-1,3-dithiol. When ethynyltriethylsilane was used, two types of products were observed: 1,2- and 2,2-double-addition products. Hydrothiolation of ethynyltriisopropylsilane by 1,3-propanedithiol led exclusively to β -dithioacetal (Scheme 5). “The steric hindrance of bulky isopropyl groups prevents the formation of 1,2-double-addition product,” suggested Mr. Kuciński.

“In summary, we have reported the highly selective hydrothiolation of unsaturated organosilicon compounds catalyzed by scandium(III) triflate. The use of allylsilanes led to products that are consistent with Markovnikov’s rule. The application of ethynylsilanes led to the formation of double-addition products – mostly β -dithioacetals. As an expansion of our method, in future we will explore its applicability to multi-unsaturated organosilicon compounds,” concluded Dr. Hreczycho.

Andreas Fank

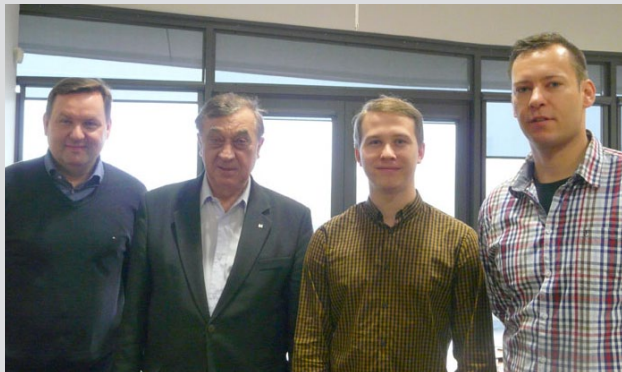


Scheme 4



Scheme 5

About the authors



From left: Dr. P. Pawluć, Prof. B. Marciniec, K. Kuciński, Dr. G. Hreczycho

Krzysztof Kuciński was born in 1989 in Inowrocław (Poland). He obtained his two BSc degrees in Spatial Economy (2011) and in Chemistry (2012), followed by his MSc degree in Chemistry (2014) at Adam Mickiewicz University in Poznań (Poland). From September to December 2012 he joined Dr. Giuliano Giambastiani's group (ICCOM-CNR Florence, Italy) as part of the Erasmus Placement Programme. In 2014 he started doctoral studies under the supervision of Dr. Piotr Pawluć. His main interests involve Lewis acids catalysis.

Piotr Pawluć received his D.Sc. (2004) and habilitation (2012) in Chemistry from the Adam Mickiewicz University in Poznań. He was a postdoctoral fellow with Professor Andre Mortreux at the Lille University (France). His research interests involve developing catalytic methodologies for the preparation of organosilicon building blocks and their application to organic synthesis.

More than 50 research publications, patents, and book chapters document his activity in the fields of organometallic chemistry, homogeneous catalysis and organic synthesis.

Bogdan Marciniec is Professor at the Faculty of Chemistry and Director of the Center for Advanced Technologies of Adam Mickiewicz University, and a member of the Polish Academy of Sciences and European Academy of Arts, Sciences and Humanities. He was Doctor honoris causa of the Łódź University of Technology (Poland) in 2013, was Dean of the Faculty of Chemistry (1985–1988) and Rector of the Adam Mickiewicz University (1988/1990), and Founder and Director of Poznań Science and Technology Park. His research is focused on the synthesis of organosilicon (also boron and germanium) compounds on the basis of new reactions and new catalysts of known reactions. He has published over 400 scientific papers, including 15 books (9 in English), 200 patents and over 17 technologies implemented in industry. He has been given the Prime Minister Award (2001), J. Śniadecki Medal (2003) of the Polish Chemical Association and the Award of the Foundation for Polish Science in technical sciences (2009) and the "Honorary Pearl" in science awarded by "Polish Market" (2009).

Grzegorz Hreczycho was born in Zielona Góra (Poland) in 1977. He obtained his D.Sc. in 2007 from the Adam Mickiewicz University under the supervision of Professor Bogdan Marciniec. His research interests cover novel applications of unsaturated silicon and germanium compounds in addition and cross-coupling reactions catalyzed by transition-metal complexes and Lewis acid catalysts.