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Journal Name

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Metal Triflates-mediated Coupling of Allylgermanes with Thiols: A Facile Route to Thiogermanes

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A novel coupling reaction of thiols with (2-methylallyl)germanes catalyzed by metal triflates has been developed. This reaction provides a direct and efficient method to afford thiogermanes and opens a valuable and general synthetic route for the Ge-S cross-coupling with elimination of isobutylene as single by-product. Scandium(III) triflate demonstrates the highest catalytic activity among of the tested triflates. All reactions were carried out under extremely mild conditions to give thiogermanes in excellent yields. This Ge-S coupling reaction shows high generality for the variety of thiols.

Germanium is well-known for its application in the electronic industry.¹ New applications for this metal as well as its compounds containing sulfur atoms are successfully developed and they are ranging from batteries,²⁻⁴ nanotechnology,^{5,6} semiconductor copolymers⁷⁻¹¹ to catalysis.¹²⁻¹⁶ Previous methods for the synthesis of the compounds containing Ge-S bond are based on cycloaddition¹⁷ or nucleophilic substitution.^{18,19} The use of chlorogermanes imposes the use of amines to neutralize hydrogen halides. The yields of the synthesized thiogermanes by the use of above-mentioned reactions are in the majority acceptable, but not excellent.

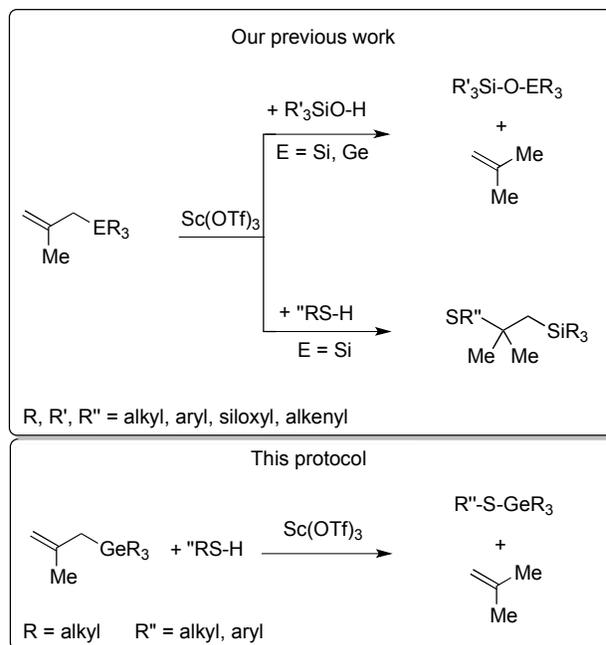
Metal triflates are classified as very selective Lewis acid catalysts. They are well-known for their unique reactivity and selectivity. What is more, the reaction conditions are very mild in most cases.²⁰⁻²¹ They have been used in cycloaddition,²²⁻²³ cycloisomerization,²⁴ carboetherification,²⁵ reduction,²⁶ cyano-methylation,²⁷ hydroxymethylation,²⁸⁻²⁹ C-H functionalization,³⁰ aldol³¹ and hydroamination reactions,³² to name a few of them.

During the course of our recent studies, we have discovered the coupling reaction of silanols and silanediols with allylsilanes, leading to SiO-Si or SiO-Ge bond formation with the evolution of isobutylene catalyzed by Sc(OTf)₃.³³⁻³⁵ The reactions proceed through catalytic O-H bond activation in silanol and cleavage of Si-C or Ge-C bond in allylmetalloid molecules (Scheme 1).

On the other hand, the Sc(OTf)₃-catalyzed reaction of allylsilanes with thiols proceeded selectively to yield hydrothiolation products, instead of Si-S coupling (Scheme 1).³⁶

In view of our recent reports on the successful use of alkenylmetaloids (Si, Ge) as new hydrogen acceptors for the O-metallation of silanols, the aim of this work was to explore the reactivity of allylgermanes in catalytic coupling with thiols leading to formation of Ge-S bond.

Here, we present a general catalytic coupling reaction that involves activation of the S-H bond in thiols by (2-methylallyl)germanes, proceeding in the presence of metal triflates, yielding selectively thiogermanes with elimination of isobutene.



Scheme 1. The reaction of silanols and thiols with allylmetaloids catalyzed by Sc(OTf)₃

We began our study by examining several triflates in the reaction with model substrates: (2-methylallyl)triethylgermane (1 equiv.)

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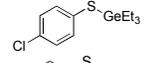
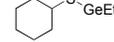
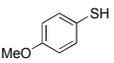
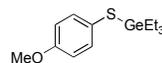
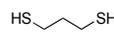
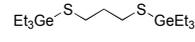
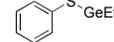
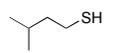
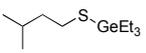
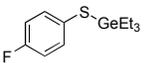
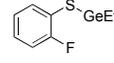
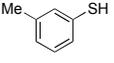
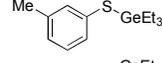
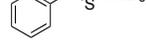
Electronic Supplementary Information (ESI) available: Full experimental details, all NMR spectra and HRMS analysis. See DOI: 10.1039/x0xx00000x

and benzenethiol (1.2 equiv.). Catalytic amounts of $\text{Sc}(\text{OTf})_3$, $\text{In}(\text{OTf})_3$, $\text{Yb}(\text{OTf})_3$, $\text{Bi}(\text{OTf})_3$ and $\text{Sm}(\text{OTf})_3$ provided different results in MeCN at room temperature. After 15 minutes we monitored progress of the reaction by using GS-MS apparatus.

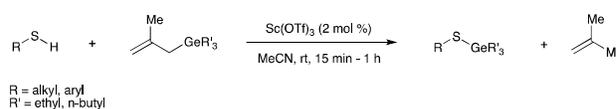
Scandium(III) triflate was found to demonstrate the highest activity in the Ge-S coupling reaction. The conversion of (2-methylallyl)triethylgermane was near to 100%. Among of triflates only samarium(III) triflate was not active in this process (2% of product after 3 days). Of other triflates all of them showed high activity in this reaction. Bismuth(III) triflate demonstrates similar activity to $\text{Sc}(\text{OTf})_3$ (92% yield of coupling product after 10 minutes), however, we observed also formation of by-product – phenyl disulfide (4%). This tendency was not change even when equimolar amounts of substrates were used. The use of indium(III) and ytterbium(III) triflates requires longer reaction time: $\text{In}(\text{OTf})_3$ (3 h, 94% yield) and $\text{Yb}(\text{OTf})_3$ (24 h, 95% yield). Taking into account the selectivity and the reaction rate, scandium(III) triflate was selected for the further synthetic procedures.

Given our optimized conditions, we investigated the scope of this reaction, using selected commercially available thiols. With the chosen catalyst in hand, we start to investigate the influence of substituents attached to sulfur. We used both aromatic and aliphatic thiols in the reaction with (2-methylallyl)triethylgermane (Scheme 2). The results are summarized in Table 1.

Table 1. Reaction of (2-methylallyl)triethylgermane with thiols catalyzed by $\text{Sc}(\text{OTf})_3$

Entry	Thiol	Product	Yield ^[a] (isolated) [%]
1			1 98 (91)
2			2 99 (93)
3			3 99 (95)
4			4 94 (90)
5			5 97 (92)
6			6 97 (91)
7			7 97 (93)
8			8 98 (92)
9			9 98 (95)
10			10 95 (92)

Reaction condition: MeCN, room temperature, 15 minutes, Germane/thiol molar ratio = 1 : 1.2 (entries 1-3 and 5-10) and 1 : 2.4 (entry 4); catalyst loading = 2 mol % (entries 1-3 and 5-10) and 4 mol % (entry 4). ^[a] Measured by GC.

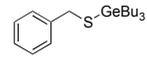
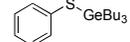
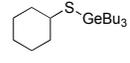
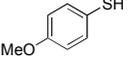
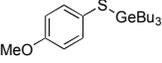


Scheme 2. The coupling reaction of thiols with (2-methylallyl)triethylgermane.

All of the applied thiols gave the expected thioether products in excellent isolated yields (90-95%). The nature of substituents at sulfur atoms proved insignificant for the reaction. What is more, aliphatic thiols demonstrates the comparable reactivity as aromatic ones. Despite the use of slight excess of thiol, only trace amounts of the competitive oxidative coupling products – disulfides were detected in the presence of $\text{Sc}(\text{OTf})_3$. All of the thioethers obtained were characterized spectroscopically. Products **1-4** and **6-8** are classified as the novel compounds.

(2-Methyl)allylgermane with *n*-butyl groups was also used in the reaction with various thiols. Representative data are summarized in Table 2.

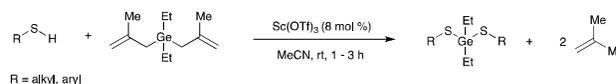
Table 2. Reaction of (2-methylallyl)tributylgermane and various thiols catalyzed by $\text{Sc}(\text{OTf})_3$

Entry	Thiol	Product	Time [h]	Yield ^[a] (isolated) [%]
1			1	93 (89)
2			0.5	98 (94)
3			0.5	96 (91)
4			1	91 (88)

Reaction condition: MeCN, room temperature, Germane/Thiol molar ratio 1 : 1.2; catalyst loading - 2 mol %. ^[a] Measured by GC.

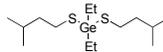
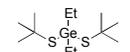
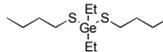
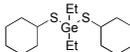
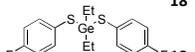
The reactivity of (2-methylallyl)tributylgermane is slightly lower than in the case of triethyl derivative. The coupling of (2-methylallyl)tributylgermane with aromatic and aliphatic thiols proceeds selectively to give thioether products with high isolated yields (88-94%), however, the total conversion of the substrate requires a longer time (0.5-1 h). The fall of reactivity is interpreted as a result of the steric hindrance of *n*-butyl groups. Products **13-14** are also classified as new compounds.

As an extension of this work, we tested di(2-methylallyl)diethylgermane in the Ge-S coupling reaction (Scheme 3). The results are summarized in table 3.



Scheme 3. The coupling reaction of thiols with di(2-methylallyl)diethylgermane

Table 3. Reaction of di(2-methylallyl)diethylgermane with thiols catalyzed by Sc(OTf)₃

Entry	Thiol	Product	Time [h]	Yield ^[a] (isolated) [%]
1			1	95 (90)
2			1	93 (88)
3			1	96 (93)
4			3	94 (89)
5			3	88 (85)

Reaction condition: MeCN, room temperature, 1–3, Germane/Thiol molar ratio: 1 : 8 (entries 1-3) and 1:5 (entries 4-5); catalyst loading, 8 mol %. ^[a] Measured by GC.

This type of compound consists of two 2-methylallyl groups is significantly less reactive in the Ge-S coupling reaction. Products were obtained with very good isolating yields (85–93%), but the catalyst loading was higher (4 mol % per allyl group) to obtain full conversion of di(2-methylallyl)germane and the reaction required longer time (1–3 h). Remarkably, the reactivity of aliphatic thiols was quite better than aromatic one. In the case of aromatic thiols, i. e. benzenethiol and 4-chlorobenzenethiol (except of 4-fluorobenzenethiol, entry 5, Table 3), we observed products of both mono and double coupling. The double coupling products were predominantly obtained with good yields 70-80% as measured by GC. However, they were contaminated by mono-coupling product (20-30%) as well as by disulfides (10-13%). Unfortunately, the increase of thiol concentration caused only the obtainment of minor amounts of disulfide product, what was not observed in the case of aliphatic thiols. Products **15-19** are also classified as novel compounds.

Conclusions

In conclusion, we have reported the new coupling reaction between thiols and (2-methylallyl)germanes leading to Ge-S bond formation with elimination of isobutylene mediated by metal triflates. Scandium triflate is the most active catalyst in this process. This highly efficient method provides facile access to aliphatic and aromatic thiogermanes, which otherwise remain challenging to be directly prepared. Mild conditions, good functional groups compatibility and the simplicity of the experimental technique are favourable features of the reaction. The obtained thiogermanes can be used for further reactions as donors of sulfanyl groups (-SR). Currently, we are working on expanding our method to multi-unsaturated organogermanium compounds.

Notes and references

General Procedures

The reagents and metal triflates used for experiments were purchased from Sigma-Aldrich Co. and ABCR GmbH & Co. KG and

used without further purification. All data connected to the synthesis of all reagents and products is collected in the supporting information file. ¹H NMR (400 MHz) and ¹³C NMR (101 MHz) were recorded on a Bruker Avance III HD NanoBay (600 MHz) spectrometer using C₆D₆ as a solvent. GC analyses were performed on a Varian 3400 with a Megabore column (30 m) and TCD. Mass spectra of products were determined by GC-MS analysis on a Varian Saturn 2100T, equipped with a BD-5 capillary column (30 m) and Finnigan Mat 800 ion trap detector. HRMS analysis were recorded on AMD 402 mass spectrometer.

Representative procedure for the coupling of (2-methylallyl)-trialkylgermanes with thiols

In 25 mL one-necked round-bottom flask, MeCN (2 mL), (2-methylallyl)trialkylgermane (0.8 mmol), thiol (0.96 mmol), and Sc(OTf)₃ (0.016 mmol; 7.9 mg) were added. The reaction mixture was stirred at room temperature for 15 minutes (for (2-methylallyl)triethylgermane) or 1 h for (2-methylallyl)-tributylgermane). The progress of reaction was monitored by GC and GC-MS analyses. After the reaction was complete, all volatiles were removed under reduced pressure. The crude product was purified by the extraction with hexane (3 mL) to give the corresponding compounds **1-14**.

The coupling of di(2-methylallyl)diethylgermane and thiols

In 25 mL one-necked round-bottom flask, MeCN (3 mL), di(2-methylallyl)diethylgermane (0.8 mmol), thiol (4 mmol or 6.4 mmol, according to Table 3), and Sc(OTf)₃ (0.064 mmol; 32 mg) were added. The reaction mixture was stirred at room temperature for 1-3 hours. The progress of reaction was monitored by GC and GC-MS analyses. After the reaction was complete, all volatiles were removed under reduced pressure. The crude product was purified by the extraction with hexane (3 mL) to give the corresponding compounds **15-19**.

Acknowledgements

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