Scandium(III) Triflate-Catalyzed *anti*-Markovnikov Hydrothiolation of Functionalized Olefins

Krzysztof Kuciński,^a Piotr Pawluć,^a and Grzegorz Hreczycho^{a,*}

^a Faculty of Chemistry, Adam Mickiewicz University in Poznań, Umultowska 89b, 61-614 Poznań, Poland E-mail: g.h@amu.edu.pl

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Dedicated to Professor Bogdan Marciniec on the occasion of his forthcoming 75th birthday in recognition of his significant contribution to organometallic chemistry.

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Abstract: Scandium(III) triflate promoted highly selective addition of thiols to functionalized olefins under mild conditions. The addition follows *anti*-Markovnikov regioselectivities, which are unusual for Lewis acids-catalyzed hydrothiolation. This reaction marks broad functional groups tolerance, which opens a beneficial synthetic route to functionalized and biologically active thio-compounds. This method is broadly applicable and offers a simple work-up in the green manner.

Keywords: alkenes; hydrothiolation; Lewis acids; scandium; synthetic methods

Introduction

Hydrothiolation of alkenes, alternatively known as thiol-ene reaction is a powerful tool for the synthesis of complex organic structures.^[1-3] This reaction has been known since 1905^[4] and allows to obtain sulfide building blocks applied as further synthetic reagents for biologically active compounds.^[5,6] Furthermore, the hydrothiolation as an example of hydroelementation reaction is compatible with the atom economy trend.^[7-11] Thus far, the S-H addition can be commonly promoted by free radical, transition metal catalysts or Lewis acids.^[12] The radical-type addition of thiols to olefins dominantly leads to the expected *anti*-Markovnikov regioisomers. In contrast, transition metal and Lewis acid catalysts leads to compounds that obey Markovnikov's rule (Scheme 1).^[9]

One of the most promising groups of Lewis acids are metal triflates. They are well-known for their



unique reactivity and selectivity under mild conditions^[13,14] and they have been used in many synthetic procedures.^[15-21] Duñach and co-workers reported the hydrothiolation of olefins catalyzed by $In(OTf)_3$. The reaction proceeds with the Markovnikov selectivity.^[22-25] The similar regioselectivity was observed by Wu and co-workers, who reported the hydrothiolation of unactivated alkenes catalyzed by $Ga(OTf)_3$.^[26] There are known other examples of that kind of regiochemistry.^[27-30]

Recently, our group discovered novel coupling reactions of allylsilanes with silanols^[31–33] and allylgermanes with silanols^[31–32] and thiols,^[34] catalyzed by scandium(III) trifluoromethanesulfonate. Sc(OTf)₃ has been also applied as the catalyst of allyl- and ethynylsilanes' hydrothiolation.^[35] In view of our recent reports, the aim of this work was to explore the reactivity of various olefins in the reaction with thiols leading to formation of the C–S bond catalyzed by scandium(III) triflate. The hypothesis assumed that resultant product will obey the Markovnikov's rule, which is common for hydrothiolation catalyzed by Lewis acids (Scheme 1).

Scheme 1. The regiochemistry of the olefin hydrothiolation

Results and Discussion

As a starting point, the reaction between linear α -olefins and 4-fluorobenzenethiol in the presence of Sc(OTf)₃ was considered. All tests were carried out in toluene, acetonitrile and under solvent-free conditions. The atmosphere effect on the reaction was also tested. In solvents, the hydrothiolation was not observed at room temperature. Next, we decided to heat up the mixture of reagents. Thus, at 80 °C the product of hydrothiolation was observed with equimolar amount of by-product - bis(4-fluorophenyl)disulfide. Under solvent-free conditions the addition product was observed within 2 h and a only trace amount of the competitive oxidative coupling product was detected (<2%). Surprisingly, we selectively obtained anti-Markovnikov regioisomer, which is unusual for the Lewis acids as the catalysts for the hydrothiolation (Scheme 2). The reaction carried out under argon atmosphere and in air gave similar results. Moreover, during the course of our studies we have discovered that our findings can be applied to a wide range of substrates from ordinary alkenes, styrenes, silylated olefins, unsaturated alcohols, alkenyl halides to unsaturated esters and functional ethers.

The results of thiols addition to unfunctionalized α -olefins are summarized in Table 1.

In all examples only *anti*-Markovnikov regioisomer was observed. Products were isolated in good yields (85–92%). We also examined the reaction between benzenethiol with 2,4,4-trimethyl-1-pentene. In this reaction two regioisomers were observed (Markovnikov : *anti*-Markovnikov, 70:30). Alkyl thiols were not reactive in this process, except for benzyl thiol. It is worth mentioning that sulfides are commonly used in oxidation processes for the synthesis of sulfoxides and sulfones.^[36,37]

The highly efficient method that provides facile access to various thio-compounds still remains a big challenge for chemists around the world, which is evidenced by the large number of publications in this subject.^[38-44] In this paper the hydrothiolation of various functional olefins is reported. The results are summarized in Table 2 and Table 3. The Sc(OTf)₃-catalyzed addition of thiols to allylsilanes was reported earlier by our group^[35] and proceeded in the Markov-nikov fashion. When the solvent (toluene or acetoni-



Scheme 2. The hydrothiolation of olefins catalyzed by $Sc(OTf)_3$

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Table 1. Sc(OTf)₃-catalyzed hydrothiolation of linear α -ole-fins^[a]



 [[]a] Reaction conditions: solvent-free, room temperature, 2h, thiol/olefin molar ratio = 1:1, catalyst loading = 2 mol%.
[b] Isolated yields.

trile) was used the isolation of the product generated from allyltrimethylsilane was unsuccessful. Surprisingly, the thiol addition to the carbon–carbon double bond carried out in solvent-free conditions occurred with *anti*-Markovnikov regioselectivity (Table 2). This is one of examples of solvent effect on regioselectivity. It is worth mentioning that the silyl-containing compounds are widely used in specific organic reactions.^[45]

The next group of functionalized alkenes were substituted styrenes. The Lewis acid-catalyzed addition of thiols to styrenes is rare due to their polymerization under acidic conditions. Benicewicz and co-workers reported the hydrothiolation of styrenes by thiols and thioacids in the presence of Montmorillonte K 10.^[46] Under catalyst-free conditions the addition of thiols in anti-Markovnikov manner was observed in benzene after 24 h. In the presence of clay the addition proceeded largely with the opposite regioselectivity. Wu and co-workers obtained similar results. They also observed the Markovnikov-type addition of thiols to styrenes catalyzed by trifluoroacetic acid.[47] In our hands, the use of scandium triflate afforded the anti-Markovnikov products in good yields (88-97%) after 1 h. We also checked the reaction between benzenethiol with α -methylstyrene. In this reaction two regioisomers were observed (Markovnikov : anti-Markovnikov, 65:35). Unfortunately, the alkyl thiols were not reactive in this process.

Encouraged by these results, we have decided to extend the generality of this reaction. Because of that, the unsaturated alcohols and alkenyl halides were treated with various thiols (Table 2). Sulfides containing hydroxy or halide groups are known as useful reagents for the synthesis of complex organic molecules.^[48–52] The addition of thiols to unsaturated alcohols proceeded with good yields (80–95%). Both,

Table 2. Sc(OTf) ₃ -catalyzed hydrothiolation of functionalized olefi
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Entr	y Thiol	Olefin	Molar ratio	Catalyst loading [mol%]	Time [h]	Product (A) ^[b]	Yield ^[c] (A) [%]	Selectivity ^[d] (A:B:C) ^[b]
1	SH	SiMe ₃	1:3	2	2	S SiMe ₃	81	98:0:2
2	F	SiMe ₃	1:3	2	2	F SiMe ₃	83	97:0:3
3	SH	Br	1:1	2	1	Br	92	100:0:0
4	SH	CI	1:1	2	1		88	100:0:0
5	Me	CI	1:1	2	1	Me of S	.CI 95	100:0:0
6	F	Br	1:1	2	1	F 9 Br	94	100:0:0
7	Me SH	Me	1:1	2	1		96	100:0:0
8	SH .	Me Contraction	1:1	2	1	S S S S S S S S S S S S S S S S S S S	97	100:0:0
9	SH	OH Me	1.2:1	2	6	12 OH S Me	87	97:0:3
10	Me	OH Me	1.2:1	3	6	Me O S O M	e 82	100:0:0
11	SH	OH Me	1.2:1	3	6	S Me	80	97:0:3
12	SH	OH Me	1.2:1	3	6	S 16 OH	80	96:0:4
13	SH .	ОН	1.2:1	2	2	S OH	95	98:0:2
14	Me	ОН	1.2:1	2	2	Me S 0	н ⁹⁴	99:0:1
15	SH	ОН	1.2:1	2	2	Състон	89	100:0:0
16	SH	Br Br	1.2:1	2	2		84	96:0:4

^[a] Reaction conditions: solvent-free, room temperature.

^[d] The selectivity was calculated by GC.

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[[]b] (A) = *anti*-Markovnikov regioisomer, (B)=Markovnikov regioisomer, (C)=Oxidative coupling product-disulfide.

^[c] Isolated yields.

Table	3. Sc(OTf) ₃ -cataly	yzed hydrothiolation of	of unsatu	irated (ethers and esters ^[a]		
Entry	Thiol	Olefin	Molar ratio	Time [h]	Product (A) ^[b]	Yield ^[c] (A) [%]	Selectivity ^[d] (A:B:C) ^[b]
1	Me O SH	P P P P P P P P P P P P P P P P P P P	1:1	5		94	99:0:1
2	F		1.2:1	5		80	97:1:2
3	F	о он	1.2:1	5	F S O OH	89	94:1:5
4	Me O SH	о он	1.2:1	5	23 Me 0 S O OH	86	97:0:3
5	SH	<i>р</i> олон	1.5:1	5	24 S O OH	80	98:0:2
6	SH Me	<i>С</i> остон	1.5:1	5	25 S S 26	84	85:0:15
7	Me	о он	1.5:1	5	Me Show OH	93	86:4:10
8	SH		1.1:1	3		96	96:0:4
9	SH	Me O Me	1.1:1	3		94	97:0:3
10	F		1.1:1	3		93	94:1:5
11	SH	O O Me	1.1:1	3	S C Me	85	97:0:3
12	F	Ph 0 Ph	1.1:1	2		89	96:0:4
13	SH	O Me	1.1:1	2		97	99:0:1

[0]

^[a] Reaction conditions: solvent-free, room temperature, catalyst loading = 2 mol%.

^[b] (A)=anti-Markovnikov regioisomer, (B)=Markovnikov regioisomer, (C)=Oxidative coupling product-disulfide.

^[c] Isolated yields.

^[d] The selectivity was calculated by GC.

alkyl and aryl thiols were reactive in this process, leading exclusively to the anti-Markovnikov adducts.

In the case of 2-propen-1-ol three products were continuously observed: dominant hydrothiolation adduct (50-60%), disulfide (30-40%) and the S-allylation product (10%). Because of that, the effect of the hydroxy group position in relation to the carboncarbon double bond was studied. It was found that

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further location of the hydroxy group favor the S-H bonds addition. On the contrary, the oxidative coupling was observed to a very minor extent (<5%)and the S-allylation products were not formed in hydrothiolation of 4-penten-2-ol and 5-hexen-1-ol (Table 2, entries 9–15). The same regioselectivity was observed when alkenyl halides were used. Allyl bromide, allyl chloride and 5-bromopent-1-ene were treated with benzenethiol. When allyl bromide was used, the mixture of products was observed in the GC-MS spectrum, including the addition product (30%). In the case of allyl chloride the product of thiol addition was observed as a predominant product (50%), but disulfide (20%) and the unidentified byproduct (30%) were also detected. The different reactivity of allyl bromide and chloride can be obviously explained by the fact, that bromide substituent is a better leaving group. When we used 5-bromopent-1ene the hydrothiolation product was obtained exclusively in the anti-Markovnikov fashion (Table 2, entry 16).

The next group of functionalized alkenes was unsaturated ethers and esters. The anti-Markovnikov products were obtained in good yields (80-97%). All results are summarized in Table 3. Functionalized sulfides containing ether or ester moieties are useful reagents for organic synthesis.^[53] The reactions of acrylates with thiols are known as the thia-Michael conjugated addition reaction.^[54-56] To our knowledge, no previous research on the reaction between unsaturated ethers containing hydroxy groups, perfluorinated ethers and allyl esters with thiols, proceeded via hydrothiolation, has been reported. Aforementioned products were obtained as dense oils that were insoluble in non-polar solvents. In the case of ethers, the presence of trace amounts of Markovnikov-type addition products was observed (<5%). On account of the insolubility of the products in non-polar solvents, the residues of disulfides were extracted by using hexane and the crude hydrothiolation adducts were purified by the column chromatography eluting with diethyl ether. This greatly simplifies the procedure for product isolation. This type of compound can be applied in the synthesis of important biologically active compounds and as further organic reagents.

The observed *anti*-Markovnikov selectivity is untypical for hydrothiolation mediated by Lewis acids. This regioselectivity may indicate that the reaction proceeds via a radical pathway. What is more, the solvent-free conditions can facilitate a radical mechanism. Because of that, we decided to carry out some tests that would answer the question about the mechanism of this process. As a starting point, the reaction between 4-penten-2-ol and benzenethiol in the absence of Sc(OTf)₃ was considered. After 24 h the hydrothiolation product was not observed. That test confirms the necessity of scandium(III) triflate as the catalyst. Previously, the effect of the atmosphere was checked and it was found that the presence of oxygen is not necessary. The important hint is the regioselectivity of the reaction between 1-decene, 4-fluorobenzenethiol and $Sc(OTf)_3$ carried out in toluene (80 °C). The MS spectra confirmed the anti-Markovnikov adduct as dominant product of the addition (88%). The comparison of MS spectra is attached in supplementary materials. The same selectivity for solvent and solvent-free conditions may suggest the existence of thiolate-intermediates. What is more, it is very interesting, that indium(III)²²⁻²⁵ and gallium(III)²⁶ triflates catalyzed the addition of S-H bond in the other way than scandium(III) triflate. The example is known where scandium and its complexes catalyze the hydroelementation in anti-Markovnikov fashion. Okuda and co-workers reported the hydrosilylation mediated by rare-earth metal complexes.⁵⁷ Goossen et al., developed anti-Markovnikov addition of imides to alkynes catalyzed by ruthenium complex and $Sc(OTf)_3$ as the co-catalyst.⁵⁸ Trifonov and co-workers also reported that ytterbium complexes are effective catalysts in anti-Markovnikov hydrophosphination and hydroamination.⁵⁹

After that, we undertook another test by using a radical scavenger. The reaction between 1-octene, benzenethiol and $Sc(OTf)_3$ in the presence of 2 mol%, 10 mol%, and 100 mol% of TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl) was considered. Nonetheless, when 2% and 10 mol% of TEMPO was used, the hydrothiolation product was smoothly obtained (80-87%). In addition, a respectable amount of disulfide was observed (13-20%). This competitive reaction was caused by TEMPO, which is often used as an oxidant in many organic procedures.60 When we used 100 mol% of TEMPO an exothermic reaction took place and we observed only 10% of adduct and 90% of disulfide.

During our work we also examined two of 1,1-disubstituted olefins (2,4,4-trimethyl-1-pentene and α methylstyrene). In both cases we observed two regioisomers with the advantage of Markovnikov's one, what may confirm the existence of ionic intermediates.

To sum up, the mechanism of the hydrothiolation is unclear. Our results may suggest that the presumable mechanism of our reaction proceed via thiolate-intermediates.

Conclusions

In conclusion, we have reported the first highly selective hydrothiolation of functionalized olefins with *anti*-Markovnikov regioselectivity catalyzed by scandium(III) triflate. Excellent isolated yields, wide functional group tolerance, short reaction time, mild sol-

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vent free-conditions, high atom economy and minimum waste generation are benefits of reported research. The hydrothiolation of ethers containing hydroxy group, perfluorinated ethers and allyl esters was achieved for the first time with excellent selectivity. Currently, we are working on expanding our method for the synthesis of the complex organic structures that show biological activity.

Experimental Section

General Procedures

The reagents used for experiments were purchased from Sigma-Aldrich Co. and ABCR GmbH & Co. KG and used without further purification. Scandium(III) triflate (99%) was purchased in Sigma-Aldrich Co. All data connected to the synthesized 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 C_6D_6 and $CDCl_3$ as solvents. 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.

Representative procedure for the synthesis of compounds 1-4, 7-12, 21

In 25 mL one-necked round-bottom flask, olefin (0.8 mmol), thiol (0.8 mmol), and $Sc(OTf)_3$ (0.016 mmol) were added. The reaction mixture was stirred at room temperature for a specific time. 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 products were purified by the column chromatography on silica gel eluting with n-hexane (compounds 1-4, 7-12) or diethyl ether (compound 21) to give the corresponding products.

Representative procedure for the synthesis of compounds 5 and 6

In 25 mL one-necked round-bottom flask, olefin (2.4 mmol), thiol (0.8 mmol), and $Sc(OTf)_3$ (0.016 mmol) were added. The reaction mixture was stirred at room temperature for a specific time. 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 products were purified by the column chromatography on silica gel eluting with *n*-hexane to give the corresponding products.

Representative procedure for the synthesis of compounds 13-20 and 22-24

In 25 mL one-necked round-bottom flask, olefin (0.8 mmol), thiol (0.96 mmol), and Sc(OTf)₃ (0.016 mmol for compounds 13, 17-20 and 22-24; 0.024 mmol for compounds 14-16) were added. The reaction mixture was stirred at room temperature for a specific time. 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 products were purified by extraction with hexane (to remove impurities) and then by the column chromatography on silica gel eluting with diethyl ether to give the corresponding products.

Representative procedure for the synthesis of compounds 25-27

In 25 mL one-necked round-bottom flask, olefin (0.8 mmol), thiol (1.2 mmol), and $Sc(OTf)_3$ (0.016 mmol) were added. The reaction mixture was stirred at room temperature for a specific time. 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 products were purified by extraction with hexane (to remove impurities) and then by the column chromatography on silica gel eluting with diethyl ether to give the corresponding products.

Representative procedure for the synthesis of compounds 28-33

In 25 mL one-necked round-bottom flask, olefin (0.8 mmol), thiol (0.88 mmol), and $Sc(OTf)_3$ (0.016 mmol) were added. The reaction mixture was stirred at room temperature for a specific time. 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 products were purified by extraction with hexane (to remove impurities) and then by the column chromatography on silica gel eluting with diethyl ether to give the corresponding products.

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