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S-Acetylation of thiols mediated by triflic acid: a novel route to thioesters

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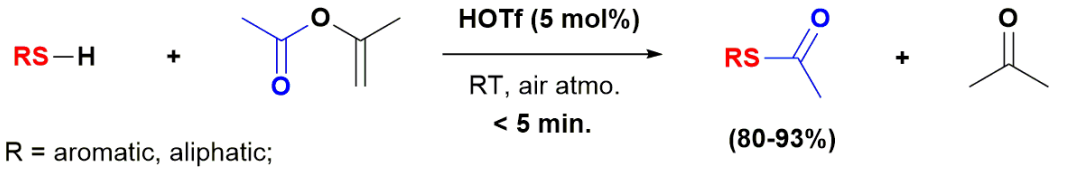

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ABSTRACT: This paper demonstrates an efficient, mild and chemoselective synthesis of various thioesters *via* a HOTf-catalyzed *S*-acetylation of aromatic and aliphatic thiols using isopropenyl acetate as a cheap and convenient acylating agent. During our tests, we also investigated the differences in the activity between metal triflates and triflic acid as catalysts in the acetylation of thiols. Finally, the potential of our concept has been increased by the implementation of Nafion® as heterogeneous catalyst of *S*-acetylation of thiols.

Keywords: S-acetylation, Thioesterification, Triflic Acid, Nafion, Thiols, Isopropenyl Acetate

Thioesters are highly important intermediates in many organic and biosynthetic transformations.[1–3] Acetyl coenzyme A is a most popular example of *S*-acetylated biomolecule that i.e., plays a vital role in fatty acid metabolism (Figure 1).[4]

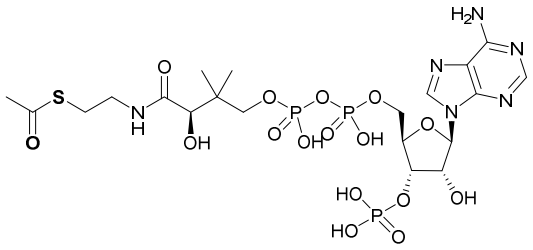
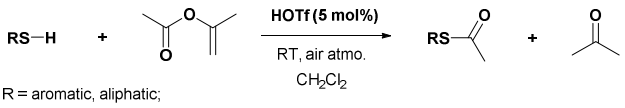


Figure 1. Structure of acetyl coenzyme A.

In this connection, thioester moiety has been extensively investigated in pharmaceutical chemistry.[5,6] Furthermore, thioesters' properties make them highly valuable reagents in organic chemistry.[7] It is also true that *S*-acylation of thiols provides an effective protection of sulfhydryl groups, which is commonly used in organic[8] and polymer chemistry.[9] There are several known methodologies for the synthesis of thioesters.[2,10–13] Carboxylic acids,[14–16] as well as acid anhydrides[17,18] and chlorides[19–22] are traditionally used as acyl sources, however the direct use of aldehydes has also been widely investigated recently in these transformations.[23–29] Nonetheless, several limitations have been observed in the above-mentioned approaches, including the use of moisture sensitive and highly reactive reagents, long reaction times, harsh reaction conditions, expensive catalysts and others. Most recently, isopropenyl acetate, which is a convenient alternative to other acetyl sources, has also been used in *N*- and *O*-acetylation.[30–32] However, its use in the absence of any catalyst is extremely rare.[32] To the best of our knowledge, the only one report has been patented,[33] which described two examples of *S*-acetylation of thiols by using isopropenyl acetate in the presence of base catalysts.

Our team has recently reported several protocols describing the use of metal triflates as the catalysts in *O*-silylation,[34–37] *O*- and *S*-germylation,[38,39] *O*-borylation,[40] *S*-benzylation,[41] *S*-*S* coupling,[42] and hydrothiolation reactions.[43,44] Triflate salts are currently widely investigated in the synthesis of organosulfur compounds[45–47] and their use in *O*- and *S*-acylation in the presence of acid anhydrides is well documented.[48–52]

In view of recent reports and literature, the aim of this work was to explore the reactivity of various thiols in the reaction with isopropenyl acetate catalyzed by metal triflates (Lewis acid catalysis). In our initial tests the chemoselectivity of this process proved to be insufficient. However, our further tests indicated that simple triflic acid is an extremely active and selective catalyst in *S*-acetylation (Brønsted acid catalysis[53,54]). In this paper, we present a highly chemoselective and efficient method for the *S*-acetylation of a variety of thiols with easily available, convenient and inexpensive isopropenyl acetate catalyzed by HOTf (Scheme 1).



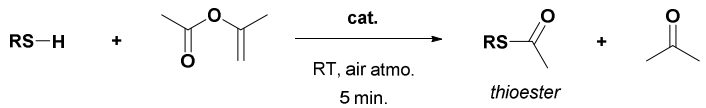
Scheme 1. *S*-acetylation of thiols mediated by HOTf.

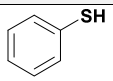
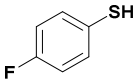
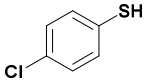
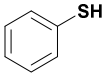
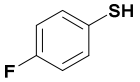
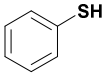
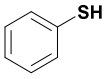
We started with the optimization of the process. Initially, benzenethiol (1.0 eq.) and isopropenyl acetate (2.0 eq.) were chosen as the coupling partners in the presence of 2 mol% of scandium(III) triflate (Table 1, entry 1). The conversion was rapid (100% of thiol after 5 minutes) and selectivity was also very good (95% of S-acetylated product). However, it was decided to also apply these reaction conditions for two other thiols (4-fluorothiophenol and 4-chlorothiophenol). In their case, the reaction was again extremely fast (less than 5 minutes), but chemoselectivity was worse than initial testing (Table 1, entries 2 and 3). Medium amounts of *C*-acylated products (35% for 4-fluorothiophenol and 10% for 4-chlorothiophenol) were first observed. We then examined a simple triflic acid (5 mol%; Table 1, entries 4 and 5), and found that the chemoselectivity for thioester formation was excellent (100%).

It is well known, that a metal triflate can serve as a source of HOTf, which may be generated *in situ via* hydrolysis.[55,56] Therefore, we performed an experiment to check which specie – triflate salt or *in situ* formed acid, was a true catalyst in this transformation. The coupling reaction between benzenethiol and isopropenyl acetate catalyzed by $Sc(OTf)_3$ was carried out with the addition of a Lewis base - 2,6-di-tert-butylpyridine (DTBP),[57] which is widely known as a proton scavenger (Table 1, entry 6). In this experiment, we observed only a small amount of C-acylated thiol and no traces of thioester. This confirmed that metal triflate was not an active catalytic specie. In the absence of a catalyst, using the same conditions, no reaction was observed (Table 1, entry 7).

To ensure maximum efficiency and selectivity, we carried out preliminary tests in a few solvents in order to choose the most suitable one (Table 1, entries 8-12). Collectively, these results indicate that CH_2Cl_2 is the best choice (Table 1, entry 4). We also tried to decrease the amount of the catalyst (for example: Table 1, entry 13), but the total conversion of thiol was not observed, even over a longer period of time. With the optimized conditions achieved, we then proceeded to examine the generality of the HOTf-mediated thioesterification. The results are summarized in Table 2.

Table 1. Reaction optimization[a]



Entry	Thiol	Solvent (1 mL)	Catalyst (mol%)	S-acetylated product[b]	C-acetylated product[b]	Disulfide[b]
1		CH_2Cl_2	$Sc(OTf)_3$ (2)	95	5	0
2		CH_2Cl_2	$Sc(OTf)_3$ (2)	55	35	5
3		CH_2Cl_2	$Sc(OTf)_3$ (2)	80	10	5
4		**CH_2Cl_2**	**HOTf (5)**	**100**	**0**	**0**
5		**CH_2Cl_2**	**HOTf (5)**	**100**	**0**	**0**
6[c]		CH_2Cl_2	$Sc(OTf)_3$ (2)	0	15	0
7		CH_2Cl_2	-	0	0	2
8		**$C_2H_4Cl_2$**	**HOTf (5)**	**100**	**0**	**0**
9		$C_6H_5CH_3$	HOTf (5)	95	3	1
10		CH_3CN	HOTf (5)	60	20	0
11		$(CH_3)_2O$	HOTf (5)	35	10	0
12		CH_3NO_2	HOTf (5)	97	3	0
13		CH_2Cl_2	HOTf (2)	80	0	1

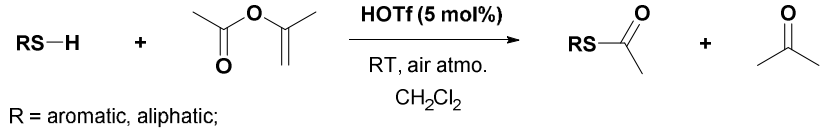
[a]Reaction conditions: room temperature, air atmosphere, thiol/isopropenyl acetate molar ratio = 1.0:2.0, reaction time = 5 min. [b]The conversion of thiols to corresponding products was calculated by GC. [c]6 mol% of 2,6-di-*tert*-butylpyridine was added.

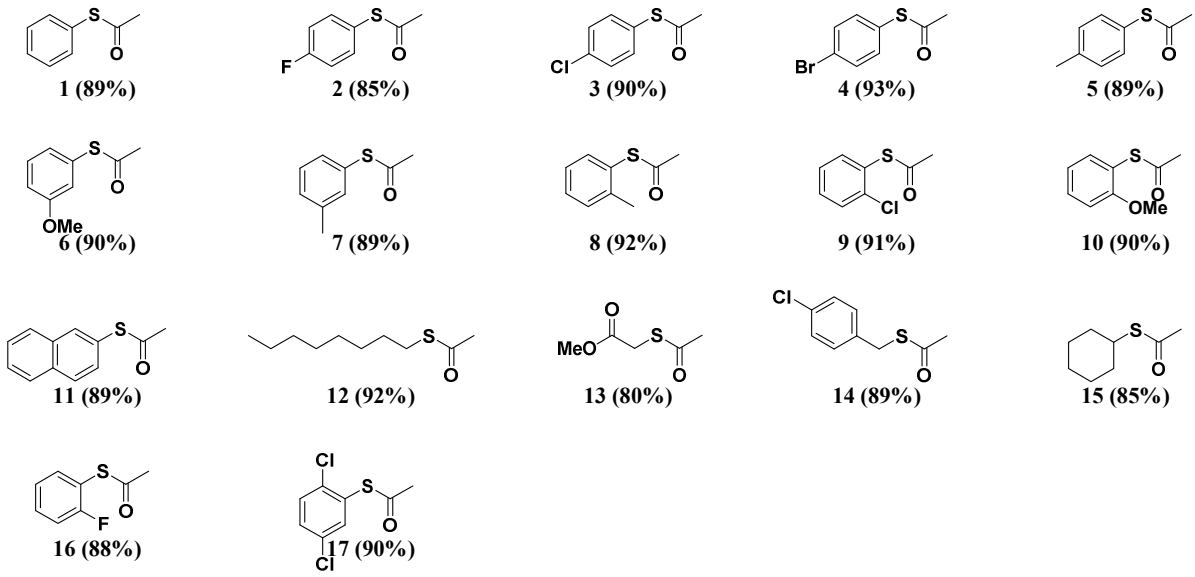
Majority of the investigated thiols were fully converted to corresponding thioesters with very good isolated yields (80-93%). In each case, the reaction was extremely fast (approx. 5 min.). Disappointedly, thiols bearing the amine (2-aminobenzenethiol, 3-aminobenzenethiol and 4-aminobenzenethiol), heterocyclic (2-thiazoline-2-thiol, 2-mercaptobenzothiazole and 2-mercapto-5-methyl-1,3,4-thiadiazole) and carboxylic (3-mercaptopropionic acid, 2-mercaptopropionic acid and thioglycolic acid) groups are not suitable to our catalytic system. Heterocyclic- and amine-substituted thiols immediately react with the catalyst, which was predictable. In the case of substrates with carboxylic groups, we observed only traces of thioesters.

Finally, the reaction of benzenethiol with isopropenyl acetate also proceeds well on a gram scale, providing *S*-phenyl thioacetate at a 91% yield level (*see Experimental Section*). On the basis of our results and the known literature, a plausible mechanism was proposed. *S*-acetylation with isopropenyl acetate can be explained as simple Brønsted acid catalysis. It assumes the activation of a carbonyl group in acidic conditions. This is followed by the attack of thiol to form an intermediate, which undergoes a rapid conversion to

thioester and corresponding enol. At room temperature an equilibrium between keto and enol form is highly shifted to ketone. Because of this, the acetone molecule is observed as the only by-product.

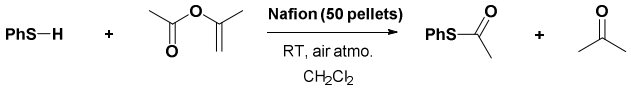
Table 2. Results for the S-acetylation of various thiols with isopropenyl acetate leading to thioesters[a]





[a]Reaction conditions: rt, 1 mL of CH_2Cl_2, air atmosphere, thiol (1.00 mmol)/isopropenyl acetate (2.00 mmol) molar ratio = 1.00:2.00, reaction time = 5 min.

The above-mentioned concept of the Brønsted acid catalysis encourage us to check a heterogeneous system based on Nafion®. This perfluorinated copolymer containing sulfonic acid groups has found use especially in alkylation[58–61] and acylation[62–64] reaction. Initially, benzenethiol (4.5 mmol) and isopropenyl acetate (9.0 mmol) were chosen as the coupling partners in the presence of 2.2 g of pellets (approx. 50) of Nafion® NR50 (Scheme 2).



Scheme 2. *S*-acetylation of benzenethiol mediated by Nafion® NR50.

To our delight, the conversion was very good (100% of thiol after 1 hour) and selectivity was also good (90% of S-phenyl thioacetate). Next, the reusability of Nafion® pellets was also examined (Figure 2). For the re-cycling test, 50 pellets were used in the same reaction conditions (4.5 mmol of benzenethiol and 9.0 mmol of isopropenyl acetate at rt). As the result, the recovered Nafion® NR50 was successfully reused without a significant loss of performance over 10 cycles (each time, 85-91% isolated yield with good selectivity (around 88-90% of S-phenyl thioacetate)).

Lastly, we performed an experiment with a column filled with Celite/Nafion® powder (ratio 3:1). Both reactants (0.05 g of benzenethiol and 0.091 g of isopropenyl acetate) were pumped through this column with 1.5 mL of CH_2Cl_2. The procedure had to be repeated 10 times to afford a high conversion. Pleasingly, under these conditions, thiophenol was selectively converted to its *S*-acylated derivative (**1**) in 90% isolated yield. In case of Nafion® powder the selectivity for *S*-acetylation (vs. *C*-acetylation) was higher (ratio 97:3). These results can contribute to further use of our catalytic system in flow chemistry[65] by using efficient flow devices.

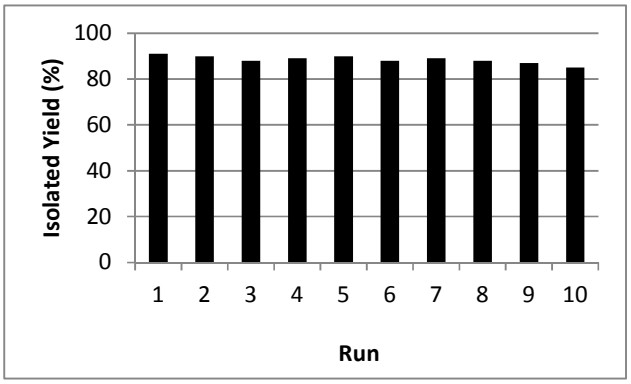


Figure 2. Recycling of Nafion® NR50 in *S*-acetylation of benzenethiol.

CONCLUSIONS

In summary, we have shown that inexpensive and readily available isopropenyl acetate can be used as a highly efficient source of acetyl group in the *S*-acetylation of various aliphatic and aromatic thiols. This reaction is mediated by simple triflic acid, which is less expensive than its metal salts. What is more, our investigations revealed that, in the case of metal triflates, they undergo hydrolysis and generated hidden Brønsted acid, which is indeed a true catalytic specie in *S*-acetylation. The favourable features of this solution are: mild conditions (rt, air atmosphere), non-toxic and non-moisture sensitive acetyl source, very good isolated yields (80-93%), high chemoselectivity (exclusively thioesters), satisfactory atom economy (acetone as the only one and recyclable by-product), and short reaction time (less than 5 min.), as well as the simplicity of the experimental techniques. Finally, the potential of our concept has been increased by the implementation of Nafion® as heterogeneous catalyst, that may also contribute to further use of our catalytic system in flow chemistry.

EXPERIMENTAL SECTION

General Information

Thiols and isopropenyl acetate used for experiments were purchased from Sigma-Aldrich Co. and used without further purification. Triflic acid was purchased from ABCR. Nafion® NR50 (pellets) and Nafion® perfluorinated resin powder were purchased from Sigma-Aldrich Co. Reactions were carried out under air atmosphere. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker Avance III HD NanoBay (400 MHz and 600 MHz) spectrometer using C_6D_6 as solvent. GC analyses were carried out on a Bruker Scion 436-GC (column: DB-5 30 m I.D. 0.53 mm) equipped with TCD. The GC yields of the crude products were calculated using decane as an internal standard. Mass spectra of few 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 thioesters (Table 2, entries 1-17):

Thiol (1.00 mmol, 1.0 eq.), isopropenyl acetate (2.00 mmol, 2.0 eq.), CH_2Cl_2 (1 mL) and triflic acid (0.05 mmol, 0.05 eq.) were added to a 10 mL one-necked round-bottom flask closed with a stopper under air atmosphere. The reaction mixture was stirred at room temperature for 5 minutes. Reaction progress was monitored by GC analyses. After the reaction was completed, in order to neutralize triflic acid the potassium carbonate (0.15 mmol, 0.15 eq.) was added. Next, the mixture was filtered over a plug of celite under suction. In next step, all volatiles (an excess amount of isopropenyl acetate, acetone (by-product) and solvent) were removed under reduced pressure and the crude product was purified by "bulb-to-bulb" distillation to give the corresponding thioesters* (Table 2, entries 1-17).

**All of the synthesized thioesters were previously reported in literature and their physical and spectral data were consistent with the ones reported in literature.*

A gram-scale synthesis of *S*-phenyl thioacetate:

To a 50 mL one-necked round-bottom flask were added benzenethiol (2.20 g, 20.0 mmol, 1.0 eq.), isopropenyl acetate (4.00 g, 40.0 mmol, 2.0 eq.), triflic acid (0.15 g, ~88 µL, 1.0 mmol, 0.05 eq.) and dichloromethane (25 mL) under air atmosphere and the flask was closed with a stopper. The reaction mixture was stirred at room temperature until monitoring of the reaction progress by GC-FID proved full consumption of benzenethiol (within 5 min.). After the reaction was completed, in order to neutralize triflic acid the potassium carbonate (3.0 mmol, 0.15 eq.) was added. Next, the mixture was filtered over a plug of celite under suction. In next step, all volatiles (an excess amount of isopropenyl acetate, acetone (by-product) and solvent) were removed under reduced pressure and the crude product was purified by "bulb-to-bulb" distillation to give S-phenyl thioacetate in 91% yield (2.77 g, 18.2 mmol).

Representative procedure for the *S*-acetylation of benzenethiol in the presence of Nafion® NR50:

Benzenethiol (4.5 mmol, 1.0 eq.), isopropenyl acetate (9.0 mmol, 2.0 eq.), CH_2Cl_2 (10 mL) and Nafion® NR50 (2.2 g, approx. 50 pellets) were added to a 50 mL one-necked round-bottom flask closed with a stopper under air atmosphere. The reaction mixture was stirred at room temperature for 1 hour. Reaction progress was monitored by GC analyses. After the reaction was completed, the solution was separated from the catalyst. Next, all volatiles (an excess amount of isopropenyl acetate, acetone (by-product) and solvent) were removed under reduced pressure to give the mixture of *S*- and *C*-acetylated products in 90% yield (Selectivity 90:10).

Recycling test in the presence of Nafion® NR50:

Benzenethiol (4.5 mmol, 1.0 eq.), isopropenyl acetate (9.0 mmol, 2.0 eq.), CH_2Cl_2 (10 mL) and Nafion® NR50 (2.2 g, approx. 50 pellets) were added to a 50 mL one-necked round-

bottom flask closed with a stopper under air atmosphere. The reaction mixture was stirred at room temperature for 1 hour. Reaction progress was monitored by GC analyses. After the reaction was completed, the solution was separated from the catalyst. Next, all volatiles (an excess amount of isopropenyl acetate, acetone (by-product) and solvent) were removed under reduced pressure to give *S*-phenyl thioacetate. Recovered Nafion® NR50 was reused in the next experiment. The catalytic performance of Nafion® NR50 was well maintained over the 10 recycling steps with yields of 85–91%.

The experiment with a column filled with Celite/Nafion® powder:

The mixture of benzenethiol (0.45 mmol, 1.0 eq.), isopropenyl acetate (0.9 mmol, 2.0 eq.) and CH_2Cl_2 (1.5 mL) were pumped through the column filled with Celite (0.564 g)/Nafion® perfluorinated resin powder (0.188 g) (ratio 3:1). The procedure had to be repeated 10 times to afford very good conversion. Next, all volatiles (an excess amount of isopropenyl acetate, acetone (by-product) and solvent) were removed under reduced pressure to give *S*-phenyl thioacetate (**1**) in 90% isolated yield.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Characterization and NMR spectra of compounds synthesized in this paper (PDF). The following files are available free of charge.

Funding Sources

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Notes

The authors declare no competing financial interest.

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