CHEMO SELECTIVE, ROOM TEMPERATURE AND SOLVENT FREE SYNTHESIS OF THIO-ESTERS USING EFFECTIVE SYNERGISTIC CATALYTIC SYSTEM

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ABSTRACT

A simple and highly efficient room temperature catalytic protocol was developed towards the synthesis of thioesters from thiols and acyl chlorides under solvent-free conditions. Ambient reaction conditions, shorter reaction time, excellent product yields are notable features of this methodology.

Keywords: Niobium Pentachloride, Silver Salt, Thiols, Acyl Chlorides.

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INTRODUCTION

The prime intention behind the development of new methodologies in synthetic organic chemistry has been the need for simple, clean and efficient strategies to obtain diverse target molecules and its analogs. Thio-esters are one of the activated carboxylic acid derivatives which act as potent acylating reagent comparable to those of acid anhydrides¹ and are vital functionality in organic transformations.² Biologically active thioesters play essential role in as indispensable metabolic intermediates in living cells owing to its ability to work as excellent acyl group transfer in biochemical reactions. In addition, natural synthesis of polypeptides and non-ribosomal polypeptides is achieved by thioester intermediates of amino and fatty acids.³

Usually thioesters are prepared by condensation of a thiols and acid chloride and they have diverse applications in synthetic chemistry as precursors to aldehydes, ketones, acids, esters, lactones, amides, lactams and heterocycles.⁴ Surprisingly, in light of diverse chemistry of thioester functionality, pave the way for combinatorial chemists to design organic molecules.⁵ Due to the significance of thioesters, a variety of chemical and enzyme-based methods have been developed for its synthesis from carboxylic acids⁶ or acid chlorides.⁷ The transformation of alkyl halides to thioesters using potassium thioacetate is reported in the literature.⁸ Recently radical initiator based azobis [2-(2-imidazoline-zolyl)] propane dihydrochloride methods are also been developed. Cetyl Trimethyl Ammonium Bromide (CTAB) as surfactant was found to be the most suitable medium for the efficient and direct synthesis thioesters the resultant aldehydes in water.⁹ Thio-esters are employed in C-C bond forming reactions and in other functional group transformations. Moreover, they demonstrate higher reactivity and selectivity towards nucleophilic substitution as compared to oxy-esters which makes them the unique acylating agent in chemical synthesis. Classically, thioesters were made from the reaction of carboxylic acids and thiols.¹⁰ The major drawback of this method is that it requires the activation of acid. Varieties of activating reagents are involved for this purpose such as trialkylthioborane,¹¹ phenyl dichloro phosphonate,¹² tri-n-butyl phosphine,¹³ diethyl phosphorocynidate¹⁴ and triphenylphosphine NBS /NIS¹⁵ and phosgene¹⁶ have been reported. Preparation of thioesters from the reaction of amides and thiols using aluminium thiophenoxide or boron thiophenoxide were also been reported in the literature.¹⁷ However, some other

methods involves use of N-methyl benzene thiazolium trifluoro methanesulfonate,¹⁸ zinc¹⁹ and thallium²⁰ tin,²¹ copper-mercaptides²² proceeds through acid chloride.²³ In recent years, cyanuric chloride²⁴ and Dess–Martin periodinane^{25–28} have been investigated to catalyze this reaction. All these methodologies have one or the other lacunas such as use of expensive reagents, tedious work-up, hazardous reagents and sometimes which generates secondary wastes.

Strong Lewis acid niobium pentachloride as a useful reagent in organic synthesis because of its stability, less hygroscopic nature and eco-friendly in handling compared to other Lewis acids. In various organic transformations are catalyzed by NbCl₅ in acyl bond and C-P bond formation reactions. We have adopted highly chemoselective method of dealkylation of alkyl aryl ethers with a stoichiometric amount of NbCl₅.²⁹ We have utilized the potentiality of NbCl₅ as a catalyst for acylation reaction as the most prominent reactions in organic synthesis.^{30–32}

EXPERIMENTAL

It is noteworthy to mention that Lewis acidity is essential for retaining the catalytic activity towards the sustainability of process in a continuous manner. The present investigation involves NbCl₅ catalyst found to be stable and catalytically robust which brings thioester conversion at room temperature in shorter time. The beneficial catalytic activity of catalyst may be due to the Lewis acidic sites present on the surface of NbCl₅ which bring activation of acid chlorides and thiols in this synthetic transformation. However, the stoichiometric amount of AgClO₄ promotes this conversion in better manner.

The solid acid NbCl₅ is found to be a better catalyst because of higher specific surface area, enhanced particle transport and generation of distinct reaction sites. Such a synthetic strategy is further modified by dispersing AgClO₄ as promoter. There are three distinct advantages: (i) its acidity can be tuned as per the organic transformations (ii) proper dispersion of reactive sites for the effective molecular collisions; (iii) solid support is effective for stronger adsorption thereby increasing the reaction rate; (iv) plausibility of its continuous usage. These methodologies are regarded as a sustainable approach.

Adopting these views, we have rationalized the highly efficient chemo selective, solvent-free synthesis of thioesters from acid chlorides and thiols in the presence of NbCl₅ and AgClO₄ as a synergistic catalyst at room temperature.

Scheme-1

General Procedure for the Synthesis of Thioester

A mixture of acid chloride (1 mmol), 1mol% of NbCl₅, 3 mol% of AgClO₄, thiol (1 mmol) was prepared and stirred at room temperature. The appearance of yellow-brown color changes to dark with the advancement of the reaction. The reaction mixture was stirred continue up to the completion of the reaction and monitored by TLC. Then it was diluted by adding DCM 10 mL, catalyst was filtered, and washed with 15 mL DCM. This extract was washed with aqueous sodium bicarbonate and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure so as to obtain pure products.

Spectral data

3a:S-phenyl benzothioate

Solid; mp 56–58°C; IR (KBr): 894, 1200, 1666, 2916, 3059 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz), δ; 7.27 - 7.63(m, 10 H, Ar-H); ¹³C NMR (CDCl₃, 100 MHz),δ; 189.9, 136.4, 135.1, 133.4, 129.4, 129.1, 128.5, 127.4, 127.3; Anal. calcd for C₁₃H₁₀SO: C, 72.86; H, 4.70; S, 14.96; Found: C, 72.85; H, 4.72; S, 14.93.

3b:S-4-Methylphenyl thiobenzoate

Solid; mp 64°C; IR (KBr): 645, 897, 1204, 1668, 2916, 3070 cm⁻¹; ¹H NMR (CDCl₃), 300 MHz), δ; 3.38 (s, 3H, Ar-CH₃), 7.22 - 7.57 (m, 5H, Ar-H), 8.00 (d, J = 7.2Hz, 2H,Ar-H), 8.10 (d, J = 7.2 Hz, 2H,ArH); Anal. calcd for C₁₄H₁₂SO: C, 73.65; H, 5.30; S, 14.04; Found: C, 73.61; H, 5.33; S, 14.01.

3c:S-Phenyl 2,2-dimethylthiopropionate

Solid; mp 33-35⁰C; IR (KBr): 645, 897, 1204, 1668, 2916, 3070 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz), δ; 1.58 (s, 9H, 3×CH₃), 7.30 - 7.68 (m, 5H, Ar-H); ¹³C NMR (CDCl₃, 100 MHz), δ; 204.4, 134.9, 129.0, 128.9, 128.0, 46.8, 27.3. Anal. calcd for C₁₁H₁₄SO: C, 67.99; H, 7.26; S, 16.50; Found: C, 67.97; H, 7.29; S, 16.47.

3d:S-4-Methylphenyl 2,2-dimethylthiopropionate

Solid; mp 38⁰C; IR (KBr): 620, 805, 929, 1473, 1695, 2930, 2966 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz), δ; 1.60 (s, 9H, 3×CH₃), 2.42 (s, 3H, Ar-CH₃), 7.99 (d, *J* = 7.4 Hz, 2H, Ar-H), 8.09 (d, *J* = 7.4 Hz, 2H, Ar-H); Anal. calcd for C₁₂H₁₆SO: C, 69.18; H, 7.74; S, 15.38; Found: C, 69.20; H, 7.71; S, 15.35.

3e:S-Phenyl thioethanoate

Oil; IR (Neat): 620, 746, 1354, 1439, 1709, 2928, 3062 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz), δ; 2.40 (s, 3H, CH₃), 7.28 - 7.76 (m, 5H, Ar-H); ¹³C NMR (CDCl₃, 100 MHz) δ = 193.8, 134.3, 129.3, 129.0, 127.8, 30.0; Anal. calcd for C₈H₈SO: C, 63.12; H, 5.30; S, 21.06; Found: C, 69.17; H, 7.73; S, 15.32.

3f:S-4-Methylphenyl thioethanoate

Oil; IR (Neat): 615, 746, 1114, 1478, 1708, 3061 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz), δ; 2.38 (s, 3H, COCH₃), 3.41 (s, 3H, Ar-CH₃), 7.97 (d, *J* = 7.2 Hz, 2H, Ar-H), 8.01 (d, *J* = 7.2 Hz, 2H, Ar-H); Anal. calcd for C₉H₁₀SO: C, 65.02; H, 6.06; S, 19.28; Found: C, 65.00; H, 6.02; S, 19.31.

3g:S-Phenyl thiocinnamate

Semi-solid; IR (Neat): 670, 895, 1605, 1680, 2900, 3029 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz), δ; 7.21 (s, 5H, Ar-H), 7.4 (s, 5H, Ar-H), 7.5 (d, 1H, *J* = 16.2 Hz, =CH), 7.62 (d, 1H, *J* = 16.2 Hz, =CH); Anal. calcd for C₁₅H₁₂SO: C, 74.96; H, 5.03; S, 13.34; Found: C, 74.98; H, 5.06; S, 13.31.

3h:S-4-Methylphenyl thiocinnamate

Oil; IR (Neat): 690, 880, 1609, 1675, 2917, 3060 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz), δ; 2.3 (s, 3H, Ar-CH₃), 7.1 (s, 5H, Ar-H), 7.4 (d, 1H, *J* = 15.5 Hz, =CH), 7.55 (d, 1H, *J* = 15.5 Hz, =CH), 7.85 (d, 2H, *J* = 7.4 Hz, Ar-H), 7.90 (d, 2H, *J* = 7.4 Hz, Ar-H); Anal. calcd for C₁₆H₁₄SO: C, 76.55; H, 5.55; S, 12.60; Found: C, 76.53; H, 5.51; S, 12.57.

3i: S-Phenyl 4-chlorothiobenzoate

Solid; mp 69⁰C; IR (KBr): 720, 916, 1171, 1588, 1665, 2970, 3035 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz), δ; 7.03 - 7.52 (m, 5H, Ar-H), 7.90 (d, *J* = 8.5 Hz, 2H, Ar-H), 8.02 (d, *J* = 8.5 Hz, 2H, Ar-H); Anal. calcd for C₁₃H₉SOCl: C, 62.77; H, 3.65; S, 12.89; Cl, 14.25; Found: C, 62.75; H, 3.63; S, 12.86; Cl, 14.27.

3j:S-4-Methylphenyl 4-chlorothiobenzoate

Solid; mp 48⁰C; IR (KBr): 740, 925, 1170, 1603, 1670, 2960, 3040 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz), δ; 2.30 (s, 3H, Ar-CH₃), 7.69 (d, *J* = 8.5 Hz, 2H, Ar-H), 7.76 (d, *J* = 8.5 Hz, 2H, Ar-H, Ar-H), 7.95 (d, *J* = 7.4 Hz, 2H, Ar-H), 8.01 (d, *J* = 7.4 Hz, 2H, Ar-H); Anal. calcd for C₁₄H₁₁SOCl: C, 63.99; H, 4.22; S, 12.20; Cl, 13.49; Found: C, 64.02; H, 4.25; S, 12.17; Cl, 13.45.

3k: S-Phenyl 1,4-dithiobenzoate

Solid; mp 58-60⁰C; IR (KBr): 751, 845, 1240, 1669, 1690, 2930, 3061 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz), δ; 7.21 - 7.54 (s, 10H, Ar-H), 7.85 (s, 4H, Ar-H); Anal. calcd for C₂₀H₁₄S₂O₂: C, 68.54; H, 4.29; S, 18.59; Found: C, 68.56; H, 4.31; S, 18.55.

3l: S-Phenyl 4-nitrothiobenzoate

Solid; mp 98⁰C; IR (KBr): 742, 850, 1220, 1670, 2918, 3062 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz), δ; 7.31-7.58 (m, 5H, Ar-H), 7.92 (d, *J* = 7.0 Hz, 2H, Ar-H), 8.03 (d, *J* = 7.0 Hz, 2H, Ar-H); ¹³C NMR (CDCl₃, 100

MHz) δ = 188.71, 151.6, 141.76, 135.6, 132.10, 129.5, 128.45, 125.11, 124.19; Anal. calcd for $C_{13}H_9SNO_3$: C, 60.22; H, 3.50; S, 12.36; N, 5.40; Found: C, 60.25; H, 3.52; S, 12.34; N, 5.41.

RESULTS AND DISCUSSION

$NbCl_5$ and $AgClO_4$ is synergistic catalyst towards highly effective and chemo selective acylation of thiols in solvent-free environment. The results are presented in (Table-1). This method is recognized to be broad or both aromatic well as aliphatic acid chlorides and brings efficient conversions with aromatic and aliphatic thiols ensuing in the formation of the consequent thioesters with better yields in shorter reaction time. This protocol is remarkably green, clean and involving no tedious work up as well as no chromatographic separation is required to obtain pure products. It is indeed to note that chemo selective acylation occurs absolutely at S atom and not on the ring carbon atom. The most interesting fact to mention that the reaction happens at room temperature is sufficient enough not promotes cleavage of ether (entry o, Table-1).

Table-1: Synthesis of Thio-esters Using $NbCl_5$ and $AgClO_4$ Catalyst under Solvent-Free Conditions

Entry	Acid Chloride	Thiol	Product	Time (min.)	Yield (%)
a				05	94
b				05	96
c				07	96
d				15	90
e				07	95
f				05	92
g				35	87
h				32	88
i				35	82
j				32	83
k				50	85
l				35	80

Entry	Acid Chloride	Thiol	Product	Time (min.)	Yield (%)
m		Et-SH		15	88
n		Et-SH		30	90
o		Et-SH		30	90
p		Et-SH		45	88
q		Et-SH		07	75
r				15	85

Even the dicarboxylic acid chloride too efficiently transformed into the consequent dithio-ester in presence of two equivalents of thiol (entry k, Table-1). The better yields are obtained during the condition when both the reactants are aromatic in nature in shorter reaction times without activation of thiols. Further, we studied the chemo selectivity the acylation by conducting the competitive acylation of phenols, alcohols, amines and thiols at ambient conditions. Interestingly, it was observed that only thiols selectively undergo acylation in presence of phenols, alcohols, and amines (Chart-I). In brief this is simple, efficient protocol towards preparation of thioesters from thiols by employing non-toxic and low-cost NbCl_5 as a catalyst without solvent at room temperature condition. The major advantages of this efficient protocol are green which comprises: simple reaction assembly not need of special equipment, less amount of catalyst is adequate to bring the conversion, ambient conditions, better yields of products with excellent chemoselectivity.

Chart-I

CONCLUSION

In conclusion, we have investigated a simple, highly efficient and chemo selective method towards acylation of thiols to provide thioesters with use of NbCl_5 and AgClO_4 as a catalyst at solvent-free condition. This is green and clean method with simple reaction set up offers excellent yields of products with short reaction times at ambient conditions with high selectivity are some of the main advantages of this protocol.

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