SHORT PAPER

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Reductive cleavage of the sulfur–sulfur bond by the samarium/Cp_2TiCl_2 used for the synthesis of S-phenyl thiolesters

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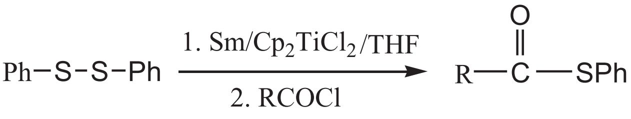
A mild method is reported for the reductive cleavage of the sulfur–sulfur bond by the samarium/ Cp_2TiCl_2 system to give a phenylthiolate anion species which reacts with acyl chlorides to give the corresponding S-phenyl thiolesters in good yields.

Keywords: sulfur–sulfur bond, samarium/ Cp_2TiCl_2, S-phenyl thiolesters

Methods for the formation of acyl–sulfur bonds are indispensable tools in synthetic chemistry. Their importance stems from the prevalence of acyl–sulfur bonds in many molecules that are of biological and pharmaceutical interest.[1] Also, thiolesters are an important class of synthetic intermediate in a variety of chemical transformations.[2] Traditional methods for the synthesis of thiolesters often require expensive, unstable and foul reagents, strong base and long reaction times. For example, the reaction between sodium thiobenzoate and arenediazonium tetrafluoroborates,[3a] the treatment of nitrosoamides or nitroamides with mercaptans in the presence of sodium hydride,[3b] the cobalt carbonyl catalysed carbonylation of mercaptans[3c] and the cobalt chloride catalysed coupling of thiols and anhydrides.[3d] We have previously reported the reduction of sulfoxides and active halides with the samarium/Cp_2TiCl_2 system.[4] In this report, we present a mild method for the reductive cleavage of the sulfur–sulfur bond with samarium/Cp_2TiCl_2 which provides a novel method for the synthesis of S-phenyl thiolesters. The sulfur–sulfur bond in diphenyl disulfide is reductively cleaved by samarium/Cp_2TiCl_2 to give a phenylthiolate anion species, which reacts with acyl chlorides to give the S-phenyl thiolesters in good yields. (Scheme 1).



$$Ph{-}S{-}S{-}Ph \xrightarrow[\text{2. RCOCl}]{\text{1. Sm/}Cp_2TiCl_2\text{/THF}} R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}SPh$$

Scheme 1

In our experiments, we discovered that when diphenyl disulfide was treated at 0 ^{0}C with samarium/Cp_2TiCl_2 the deep blue-green colour of the solution turned into brownish red within several seconds. The above appearance indicated the sulfur–sulfur bond had been reductively cleaved and the phenylthiolate anion species was formed. Addition of acyl chlorides lead to the formation of S-phenyl thiolesters. The results are summarised in Table 1.

In summary, we have reported a mild method for the reductive cleavage of sulfur–sulfur bond and the synthesis of S-phenyl thiolesters. The advantages of our method are single product formation, simple manipulation, and mild and neutral conditions.

Table 1 The reductive cleavage of sulfur-sulfur bond induced by samarium/Cp_2TiCl_2

Entry in R–S–SR	R	Product	Yield/%[a]
a	Ph	PhCOSPh	74
b	3-ClC_6H_4	3-ClC_6H_4COSPh	79
c	2-BrC_6H_4	2-BrC_6H_4COSPh	68
d	PhCH=CH	PhCH=CHCOSPh	62
e	$CH_3(CH_2)_4$	$CH_3(CH_2)_4$COSPh	91
f	$CH_3(CH_2)_{10}$	$CH_3(CH_2)_{10}$COSPh	80

[a]See Experimental.
[b]Isolated yields based on diphenyl disulfide.

Experimental

Melting points were uncorrected. The tetrahydrofuran was freshly distilled from sodium/benzophenone ketyl prior to its use. All the compounds were characterised by IR and NMR spectra.

General procedure: Samarium powder (0.3g, 2mmol) and Cp_2TiCl_2 (1g, 4mmol) were placed in a well-dried three-necked round bottom flask containing a magnetic stirrer bar. The flask was flushed several times with dinitrogen, and then tetrahydrofuran (15ml) was added through a rubber septum by a syringe. The resulting mixture was stirred at 70 ^{0}C for 0.5h. The deep blue-green solution formed was cooled to 0 ^{0}C on a ice bath and a solution of diphenyl disulfide (2mmol) in anhydrous THF (2ml) was added. The deep blue-green colour of the solution changed to a brownish red within several seconds. Then the ice bath was removed and the reaction mixture was warmed to room temperature. Acyl chloride (4mmol) in anhydrous THF (2ml) was added and stirred at room temperature for 2h. The reaction was monitored by TLC. The reaction mixture was diluted with diethyl ether (60ml) and filtered. The filtrate was washed with brine (3 × 30ml). After the solution was dried over anhydrous magnesium sulfate, the solvent was removed under reduced pressure. The crude product was purified by preparative TLC on silica gel (petroleum ether as eluent). The products were identified by m.p. IR and ^{1}H NMR spectra.

a: m.p. 54–55 ^{0}C (lit.[5] 53–54 ^{0}C); ν_{max} (KBr)/ cm^{-1} 1691 (C=O); δ_H ($CDCl_3$/TMS): 7.27 (8H, m), 7.80(2H, m).

b: m.p. 40–41 ^{0}C (lit.[5] 40–41 ^{0}C); ν_{max} (KBr)/ cm^{-1} 1706 (C=O); δ_H ($CDCl_3$/TMS): 7.30 (7H, m), 7.87(2H, m).

c: m.p. 49–51 ^{0}C (lit.[6] 49–51 ^{0}C); ν_{max} (KBr)/ cm^{-1} 1705 (C=O); δ_H ($CDCl_3$/TMS): 7.33 (9H, m).

d: m.p. 77–78 ^{0}C (lit.[7] 76–78 ^{0}C); ν_{max} (KBr)/ cm^{-1} 1695 (C=O); δ_H ($CDCl_3$/TMS): 6.73 (1H, d), 7.38 (1H, d), 7.27 (10H, m).

e: oil (lit.[8]); ν_{max} (KBr)/ cm^{-1} 1723 (C=O); δ_H ($CDCl_3$/TMS): 0.90 (3H, t), 1.13–1.87 (6H, m), 2.55 (2H, t), 7.30 (5H, s).

f: oil (lit.[9]); ν_{max} (KBr)/ cm^{-1} 1725 (C=O); δ_H ($CDCl_3$/TMS): 0.87 (3H, t), 1.25–1.87 (18H, m), 2.55 (2H, t), 7.25(5H, s).

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

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