

Reductive Cleavage of S-S Bond by Samarium Diiodide: Synthesis of β -Thioesters and β -Thionitriles

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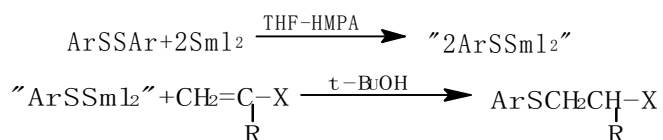
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Abstract: The reduction of disulfides by samarium diiodide led to samarium thiolates (ArSSmI_2). This new thiolate anion species reacted smoothly with α , β -unsaturated esters (nitriles) to give 1, 4-addition products β -thioesters and β -thionitriles in good yields under mild and neutral condition.

Keywords: β -thioesters, β -thionitriles, samarium diiodide, synthesis.

The use of samarium diiodide as a strong one-electron transfer reducing and coupling reagent in organic synthesis has gained increasing popularity, especially in the past ten years¹. Our previous work on some deoxygenation and some reductive cleavage of Se-Se or Te-Te bond with SmI_2 was reported². Since the S-S bond energy is only 50.9 Kcal/mol, this led us to investigate the reductive cleavage of S-S bond by SmI_2 . Most reducing agents for symmetrical disulfides are strong bases or Se-CO-H₂O system³. But SmI_2 is an efficient, mild and neutral reducing agent. Here we wish to report the preparations of samarium thiolate which are good intermediates for the synthesis of β -thioesters and β -thionitriles via 1, 4-addition reaction with α , β -unsaturated esters and α , β -unsaturated nitriles under mild and neutral conditions.

We found that under mild conditions, treatment of disulfide with two equivalents of SmI_2 in THF-HMPA system resulted that the S-S bond had been reductively cleaved by SmI_2 and that the trivalent samarium species had been formed. We assumed that this trivalent samarium species was the samarium thiolates (ArSSmI_2). The samarium thiolates reacted smoothly with α , β -unsaturated esters and α , β -unsaturated nitriles to give β -thioesters and β -thionitriles in good yields. The results are summarized in **Table 1**.



Ar: Ph, PhCH₂;

X: CN, COOMe, COOEt, COOB_{U-n}; R: H, CH₃;

Table 1. Reductive Cleavage of S-S Bond by SmI₂: Synthesis of β -Thioesters and β -Thionitriles.

NO	substrate	olefin	Product	yield (%)
1	PhSSPh	CH ₂ =CH-CN	PhSCH ₂ CH ₂ CN	80
2	PhSSPh	CH ₂ =CH-COOMe	PhSCH ₂ CH ₂ COOMe	87
3	PhSSPh	CH ₂ =CHCOOEt	PhSCH ₂ CH ₂ COOEt	93
4	PhSSPh	CH ₂ =CHCOOBu-n	PhSCH ₂ CH ₂ COOBu-n	84
5	PhSSPh	CH ₂ =C (CH ₃)COOMe	PhSCH ₂ CH (CH ₃)COOMe	81
6	PhSSPh	CH ₂ =C (CH ₃)COOEt	PhSCH ₂ CH (CH ₃)COOEt	80
7	PhCH ₂ SSCH ₂ Ph	CH ₂ =CHCN	PhCH ₂ SCH ₂ CH ₂ CN	70
8	PhCH ₂ SSCH ₂ Ph	CH ₂ =CHCOOMe	PhCH ₂ SCH ₂ CH ₂ COOMe	63
9	PhCH ₂ SSCH ₂ Ph	CH ₂ =CHCOOEt	PhCH ₂ SCH ₂ CH ₂ COOEt	83
10	PhCH ₂ SSCH ₂ Ph	CH ₂ =CHCOOBu-n	PhCH ₂ SCH ₂ CH ₂ COOBu-n	80
11	PhCH ₂ SSCH ₂ Ph	CH ₂ =C (CH ₃)COOMe	PhCH ₂ SCH ₂ CH (CH ₃)COOMe	73

a) The products were fully characterized by their ¹H NMR and IR spectra.

b) Isolated yield.

Experimental

A representative procedure for the synthesis of β -thioester and β -thionitrile:

The deep blue solution of SmI₂ (2.2 ml) in THF (22 ml) was added HMPA (1 ml) and the solution became deep purple. Disulfide (1 mmol) was added at room temperature under nitrogen atmosphere. The mixture was stirred for 1.5 hours. To the mixture was added successively α , β -unsaturated ester or nitrile (2mmol) and t-BuOH (2mmol); then stirred at room temperature for 3 hours. The reaction mixture was added hydrochloric acid (10 ml) and was extracted with ether (20 ml×2), the combined organic extracts were successively washed with brine (10 ml), aqueous Na₂S₂O₃ (10 ml) and brine (10 ml). The organic layer was dried with MgSO₄, filtered and the solvent removed in vacuo. The crude product was then purified by TLC on silica gel (ether:petroleum=1:5) to give colourless liquid.

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