Reductive Cleavage of S-S Bond by Sm/$NiCl_2$ or Sm/$NiCl_2 \cdot 6H_2O$ System : A New Method for the Preparation of Thiolesters

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Abstract: Disulfides were reduced by the Sm/$NiCl_2$ or Sm/$NiCl_2 \cdot 6H_2O$ system to generate thiolate anion , which reacted further with anhydrides or acyl chlorides to afford thiolesters in good yields under mild and neutral conditions.

Keywords : Samarium-nickel (II) chloride, disulfide, thiolester.

The role of thiolesters as acylating agents in biochemical processes and their high reactivity with various nucleophiles, has made them an attractive synthetic inter mediate in organic synthesis[1-3]. Many new methods have been developed for the preparation of thiolesters in recent years[4-11], for example, the reaction between sodium thiobenzoate and arenediazonium tetrafluoroborates[6], treatment of nitrosoamides or nitroamides with mercaptans in the presence of sodium hydride[8], the cobalt carbonyl catalyzed carbonylation of mercaptans[9] and the cobalt chloridecatalyzed coupling of thiols and anhydrides[11].

As a powerful, versatile and ether-soluble one-electron transfer reducing agent, SmI_2 has been widely applied in organic synthesis[12]. Though SmI_2 is a useful reagent, storage is difficult because it is very sensitive to air oxidation. On the other hand, metallic samarium is stable in air and its strong reducing power ($Sm^{3+}/Sm=-2.41V$) is similar to that of magnesium ($Mg^{2+}/Mg=-2.37V$) and superior to that of zinc ($Zn^{2+}/Zn=-0.71V$). These properties prompted us to use the more convenient and cheaper samarium directly as a reductant in stead of samarium (II) iodide.

Our previous work on the reductive cleavage of C-S and S-S bond by SmI_2 to give thiolesters has been reported[13-14]. Here we wish to report that the disulfides were reduced by the $Sm/NiCl_2$ system to generate thiolate anion, which reacted further with anhydrides or acyl chlorides in THF under mild and neutral conditions (**Scheme 1**) to afford thiolesters in good yields. The results are summarized in **Table 1**. It is interesting that we also found that disulfides by the $Sm/NiCl_2 \cdot 6H_2O$ system could react with anhydrides or acyl chlorides to give thiolesters in good yields under the same conditions as above. The results (listed in **Table 2**) of our experiments indicated that such a small amount of water in $NiCl_2 \cdot 6H_2O$ showed no notably bad influence on the reaction, but it could make the operation more convenient and simpler. Some control experiments revealed that S-S bond could be cleaved neither by Sm nor by $NiCl_2$ alone.

In conclusion, it has been found that the $Sm/NiCl_2$ or $Sm/NiCl_2 \cdot 6H_2O$ system can be used for the preparation of thiolesters *via* the reductive cleavage of the S-S bond at mild temperature. The advantages of this reaction are neutral reaction condition, simple operation and good yields.

Scheme 1

$$\mathrm{RSSR} + \underset{(X=Cl,\ OCOR^1)}{\mathrm{R^1COX}} \xrightarrow[\text{or } Sm/NiCl_2 \bullet 6H_2O]{Sm/NiCl_2} \mathrm{RSCOR^1}$$

Table 1 Reaction with $Sm/NiCl_2$ system*

Entry	R	R^1	X	Product	Yield**(%)
1	C_6H_5	CH_3	$OCOCH_3$	$C_6H_5SC(O)CH_3$	78
2	C_6H_5	$CH_2CH_2CH_3$	$OCOCH_2CH_2CH_3$	$C_6H_5SC(O)CH_2CH_2CH_3$	81
3	C_6H_5	C_6H_5	Cl	$C_6H_5SC(O)C_6H_5$	77
4	C_6H_5	C_6H_5	$OCOC_6H_5$	$C_6H_5SC(O)C_6H_5$	67
5	C_6H_5	$(CH_2)_4CH_3$	Cl	$C_6H_5SC(O)(CH_2)_4CH_3$	70
6	C_6H_5	$(CH_2)_{10}CH_3$	Cl	$C_6H_5SC(O)(CH_2)_{10}CH_3$	70
7	$C_6H_5CH_2$	CH_3	$OCOCH_3$	$C_6H_5CH_2SC(O)CH_3$	61
8	$C_6H_5CH_2$	$CH_2CH_2CH_3$	$OCOCH_2CH_2CH_3$	$C_6H_5CH_2SC(O)CH_2CH_2CH_3$	53

Table 2 Reaction with Sm/NiCl$_2$ • $6H_2O$ system*

Entry	R		X	Product	Yield**(%)
1	C_6H_5	CH_3	$OCOCH_3$	$C_6H_5SC(O)CH_3$	77
2	C_6H_5	CH_2CH_3	Cl	$C_6H_5SC(O)CH_2CH_3$	71
3	C_6H_5	$CH_2CH_2CH_3$	$OCOCH_2CH_2CH_3$	$C_6H_5SC(O)CH_2CH_2CH_3$	75
4	C_6H_5	$(CH_2)_4CH_3$	Cl	$C_6H_5SC(O)(CH_2)_4CH_3$	71
5	C_6H_5	$(CH_2)_{10}CH_3$	Cl	$C_6H_5SC(O)(CH_2)_{10}CH_3$	63
6	C_6H_5	C_6H_5	Cl	$C_6H_5SC(O)C_6H_5$	70
7	$C_6H_5CH_2$	CH_3	$OCOCH_3$	$C_6H_5CH_2SC(O)CH_3$	58

*All products were characterized by ^{1}H NMR and IR. **Isolated Yields.

General Procedure

Under a nitrogen atmosphere, metallic samarium powder (1.0 mmol) , NiCl$_2$ or NiCl$_2$ • $6H_2O$ (1. 0 mmol) and disulfides (0. 5 mmol) were placed in a three necked reaction flask and THF (10 ml) was added in one portion. Anhydride or acyl chloride (1. 2 mmol) was then added to the mixture and stirred at 50 ℃ for 5 h. A dilute solution of HCl was added to quench the reaction and the mixture was extracted with diethyl ether (20 ml×2). The organic layer was washed with water (20 ml×2) and dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo*. The residue was then purified by preparative TLC on silica gel (cyclohexane-ethyl acetate as eluent) to give pure product.

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References

1. O. Yoshiyuki, T. Masanori, K. Masaaki, and I. Yoshio, *Uakromol. Chem. Rapid. Cornmun.*, **1991**, *12*, 465.
2. M. F. El-Zohry, A. M. El-Khawaga, M. T. Ismail, and A. A. Abdel-Wahab, *Phosphorus Sulfur Silicon Relat. Elem.*, **1991**, *61*, 373.
3. A. Waldemar, and H. Lazaros, *Tetrahedron Lett.*, **1992**, *33*, 469.
4. F. Isao, T. Naomi, and H. Shizunobu, *Chem. Express*, **1989**, *4*, 337.
5. J. Y. Gauthier, F. Bourdon, and N. Young, *Tetrahedron Lett.*, **1986**, *27*, 15.
6. P. Giovanni, N. Marino, G. Giacomo, and F. Marcos, *Tetrahedron*, 1989, *45*, 7411.
7. Y. V. Gulevich, N. A. Bumagin, and Z. P. Beletskaya, *Zh. Org. Khim.*, **1988**, *24*, 2126.
8. B. Ramon, G. Jordi, and V. Jaume, *Synthesis*, **1989**, *4*, 305.
9. A. Shlomo, and A. Howard, *Organometallic*, **1986**, *5*, 596.

10. C. Cardellicchio, V. Fiandanese, G. Marchese, and L. Ronzini, *Tetrahedron Lett.*, **1985**, 26, 3595.
11. A. Saeed, and i. Javed, *Tetrahedron Lett.*, **1986**, *27*, 3791.
12. a) H. B. Kagan, and J. L. Namy, *Tetrahedron,* **1986**, *42*, 6573.
    b) G. A. Molander, *Chem. Rev.*, **1992**, *92*, 29.
    c) G. A. Molander, *Org. React.*, **1994**, *46*, 211.
    d) G. A. Molander, and C. R. Harris, *Chem. Rev.*, 1996, *96*, 307.
13. X. Jia, Y. Zhang, and X. Zhou, *Tetrahedron Lett.*, **1994**, *35*, 8833.
14. X. Jia, Y. Zhang, and X. Zhou, *Synth. Commun.*, **1994**, *24*, 387.
15. P. A. Griceo, Y. Yokyama, and E. Williams, *J. Org. Chem.*, **1978**, *43*, 1283.

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