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Reductive Cleavage Of C—S Bond By Samarium Diiodide: A Novel Method For The Synthesis Of Disulfides And Thiolesters

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Abstract: Disulfides were obtained by the reaction of thiocyanates with equivalent SmI_2. Samarium thiolates were generated by the reaction of an equivalent of thiocyanates with two equivalents of SmI_2, and then reacted smoothly with acyl chlorides to give thiolesters.

Samarium diiodide as a powerful one electron transfer reducing agent has extensively been applied to organic synthesis in the last decade.[1] We have recently reported the reduction of elemental selenium with SmI_2 and the reductive cleavage of S—S bond in diphenyl disulfide by SmI_2.[2]

Both disulfides[3] and thiolesters[4] are useful synthetic intermediate in a variety of chemical transformations, and many methods have been developed for the preparation of disulfides[5] and thiolesters.[6] Here we wish to report a novel synthetic approach of disulfides and thiolesters from the reductiion of thiocyanates mediated by samarium diiodide.

$$\underset{1}{\text{R-S-CN}} \xrightarrow{SmI_2} \underset{2a-g}{\text{R-S-S-R}}$$

2a: $R=n\text{-}C_5H_{11}$ 80%
2b: $R=n\text{-}C_6H_{13}$ 78%
2c: $R=n\text{-}C_7H_{15}$ 73%
2d: $R=n\text{-}C_8H_{17}$ 70%
2e: $R=n\text{-}C_{10}H_{21}$ 85%
2f: $R=n\text{-}C_{12}H_{25}$ 75%
2g: $R=n\text{-}C_{16}H_{33}$ 76%

$$\underset{1}{\text{R-S-CN}} \xrightarrow{2SmI_2} \underset{3}{\text{“}RSSmI_2\text{”}} \xrightarrow{R'COCl} \underset{4a-h}{RSCOR'}$$

4a: $R=CH_3(CH_2)_6$, $R'=Ph$ 81%
4b: $R=CH_3(CH_2)_9$, $R'=Ph$ 72%
4c: $R=CH_3(CH_2)_5$, $R'=CH_3(CH_2)_4$ 79%
4d: $R=CH_3(CH_2)_5$, $R'=CH_3(CH_2)_{10}$ 67%
4e: $R=CH_3(CH_2)_6$, $R'=CH_3(CH_2)_{10}$ 68%
4f: $R=CH_3(CH_2)_7$, $R'=CH_3(CH_2)_{10}$ 76%
4g: $R=CH_3(CH_2)_9$, $R'=CH_3(CH_2)_{10}$ 83%
4h: $R=CH_3(CH_2)_{11}$, $R'=CH_3(CH_2)_{10}$ 71%

The thiocyanates used as starting substrates were prepared by the reaction of alkyl bromides with potassium thiocyanate in refluxing ethanol.[7] When thiocyanates reacted with equivalent SmI_2 in THF, the deep blue color of SmI_2 disappeared within 10—15 minutes, which showed that the reaction had been completed. The products were disulfides and no by-products were observed by means of TLC. However, when an equivalent of thiocyanates reacted with two equivalents of SmI_2 in THF, the deep blue color of SmI_2 disappeared within 1—2.5h, and subsequent addition of acyl chlorides resulted in thiolesters. It was indicated that samarium thiolates had been generated in situ.

According to the above facts and our previous work,[2] we consider that the reason why the reaction of thiocyanate with equivalent SmI_2 was stopped at the disulfide stage may have two aspects: i) there is no excess samarium diiodide in the reaction; ii) the rate of formation of disulfide is faster than that of cleavage of S—S bond in disulfide.

We have developed a novel approach for the synthesis of disulfides and thiolesters from the reduction of thiocyanates by samarium diiodide. It is speculated that samarium diiodide may transfer one electron to thiocyanate to form the radical anion$(R-S-CN)^{\overline{\cdot}}$, which was cleaved into $RS\cdot$ and CN^-. The coupling of the radical $RS\cdot$ gives disulfide. In the presence of excess samarium diiodide, the radical $RS\cdot$ may receive an electron to generate thiolate anion RS^-, which smoothly reacted with acyl chlorides to give thiolesters.

General procedures are as follows:

Preparation of disulfides. Alkyl thiocyanate(2mmol) was added at room temperature under nitrogen to the deep blue solution of SmI_2(2.2 mmol) in THF(22ml). The solution turned into dark brown in 10—15 minutes. The reaction mixture was then diluted with ether and filtered. The ethereal solution was washed with water, dried over $MgSO_4$ and evaporated to give crude product. The crude product was then purified by preparative TLC on silica gel (cyclohexane as eluent).

Preparation of thiolesters. Alkyl thiocyanate(1mmol) in THF(1ml) was added to the deep blue solution of SmI_2(2.2mmol) in THF(22ml) at room temperature under nitrogen. After the mixture was stirred for 1—2.5h, acyl chloride(1.5mmol) in THF(1ml) was added and stirred for 2h, and then treated in above manner to give the product.

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