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A novel reduction of sodium alkyl thiosulfates using samarium metal without an activating agent in water

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Abstract—A novel metallic samarium promoted reduction of sodium alkyl thiosulfates in the absence of an activating agent occurs to afford the corresponding disulfides with good yields in water at 90°C. © 2002 Elsevier Science Ltd. All rights reserved.

Samarium metal, its salts and organosamarium compounds have recently been widely employed as useful reagents or catalysts in organic synthesis.[1] Since the pioneering studies by Kagan and his co-workers demonstrated the particular effectiveness of samarium(II) iodide (SmI_2) as a powerful one-electron transfer reductant,[2] the utilization of SmI_2 in synthetic organic synthesis has been dramatically documented.[3] Though SmI_2 is a useful reagent, some problems are encountered when it is used as a reductant. For example, it is expensive and it needs delicate treatment and careful storage because it is very sensitive to air oxidation. On the other hand, metallic samarium is stable in air and has stronger reducing power ($Sm^{3+}/Sm = -2.41$ V) than that of SmI_2 ($Sm^{3+}/Sm^{2+} = -1.55$ V) and it has been noted recently that the cheaper and more convenient metallic samarium can be used directly as a reductant instead of SmI_2 in organic synthesis.[4] Because the samarium atoms on the accessible solid surface are not sufficiently reactive,[5] suitable activating agents, such as $HgCl_2$,[6] TMSCl,[7] NH_4Cl (aq.),[8] I_2[9] or 1,1′-dioctyl-4,4′-bipyridinium dibromide[10] have been used to activate metallic samarium to promote the reaction.

Metal-mediated organic reactions in aqueous media have received considerable attention in organic synthesis over the last decade.[11] Such reactions in aqueous media offer a number of advantages over conventional organometallic reactions in organic solvents. They are environmentally friendly and practically convenient. However, because of the lower solubility of most organic compounds in water, these reactions and their applications are limited to a great extent.

Disulfides are important reagents and intermediates in organic synthesis,[12] and many methods for the synthesis of disulfides have been recommended, for example, the oxidation of thiols[13] and nucleophilic substitution of sulfenylthiocyanates,[14] thiolsulfonates,[15] sulfenylhydrazo compounds,[16] and sulfenimides[17] with thiols, and the reduction of sulfonic acids and sodium sulfonates,[18] and sulfenyl, sulfinyl and sulfonyl derivatives,[19] etc. However, these methods suffer from using either foul-smelling thiols, or harsh reaction conditions, in addition to only moderate yields and waste handling problems. It is desirable to develop milder and environmentally friendly methods for the preparation of disulfides.

The first ionization potential of metallic samarium is 5.63 eV, similar to that of metallic indium (5.79 eV) and lithium (5.39 eV). This property prompted us to use hot water to react with metallic samarium (the surface of samarium is inactive in cold water!). Also we considered the fact that sodium alkyl thiosulfates have a great solubility in hot water. Here, we wish to report a novel reduction of sodium alkyl thiosulfates by using metallic samarium in water at 90°C, which occurs to afford the corresponding disulfides in good yield.

$$\mathrm{RSSO_3Na} \xrightarrow[90^\circ\mathrm{C}]{\mathrm{Sm/H_2O}} \mathrm{RSSR}$$

Our initial experiments explored the effect of the reaction temperature on the reduction of sodium alkyl

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Keywords: samarium metal; sodium alkyl thiosulfates; hot water; reduction; disulfides.

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thiosulfates mediated by metallic samarium in water. The results are summarized in Table 1. Sodium dodecyl thiosulfate was chosen as the model compound for this investigation.

From Table 1, it is evident that the reaction temperature plays a very important role in the reductive coupling of sodium alkyl thiosulfates. When the reaction temperature is below 50°C the reduction occurs with difficulty because of the inactivity of the metallic samarium surface, and when the reaction temperature is above 120°C, the reaction of samarium powder with water is so fast that the reduction of sodium alkyl thiosulfate is not complete. The most effective reaction temperature is between 85 and 100°C. A reaction temperature of 90°C was chosen for further study.

A variety of sodium alkyl thiosulfates was successfully reduced with metallic samarium followed by self-coupling to afford the corresponding disulfides in water (90°C) without any activator. The results are listed in Table 2.

The data in Table 2 show that sodium alkyl thiosulfates can be easily reduced to the corresponding symmetrical disulfides by metallic samarium powder in near boiling water with good yields. The chain length of aliphatic substrates would seem to have no influence on the reductive coupling reaction. Substituent effects were also examined in a series of sodium benzyl thiosulfates. The results indicated that the reaction is relatively insensitive to the electronic nature of substituents on the aromatic rings. It is noteworthy that a substrate with a nitro group on the aromatic ring requires a longer time to complete the reaction and the nitro group is unchanged after the reaction (Table 2, entry 12). As the starting material, the sodium alkyl thiosulfates are readily prepared from the reaction of sodium thiosulfate with a suitable alkyl bromide under mild phase transfer catalysis conditions.[20]

Typical procedure: The synthesis of di(n-dodecyl)disulfide is representative. Under an inert atmosphere of nitrogen, samarium powder (1 mmol) and sodium alkyl thiosulfate (1 mmol) were placed in a round-bottomed flask, and water (5 mL) was added in one portion. The mixture was stirred at 90°C for 4 h. After cooling, the product was extracted with ether (2×20 mL). After the organic layer was dried over anhydrous sodium sulfate, the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel using hexane/ethyl acetate as eluting agent to give di(n-dodecyl)disulfide (181 mg, 90% yield).

Table 1. Effect of reaction temperature on the reductive coupling of sodium dodecyl thiosulfate in water[a]

Entry	Temp. (°C)	Time (h)	Yield (%)[b]
1	25	24	0
2	50	24	0
3	75	4	52
4	85	4	85
5	90	4	90
6	100	4	88
7	120	4	45
8	150	4	12

[a] Reaction conditions: metallic samarium powder (1 mmol), sodium dodecyl thiosulfate (1 mmol), water (5 mL).

[b] Isolated yields.

Table 2. The reduction of sodium alkyl thiosulfates to disulfides by metallic samarium in 90°C water[a]

Entry	Reactant	Time (h)	Product[b]	Yield (%)[c]
1	n-$C_{16}H_{33}SSO_3Na$	4	(n-$C_{16}H_{33}S)_2$	91
2	n-$C_{12}H_{25}SSO_3Na$	4	(n-$C_{12}H_{25}S)_2$	90
3	n-$C_{10}H_{21}SSO_3Na$	4	(n-$C_{10}H_{21}S)_2$	85
4	n-$C_8H_{17}SSO_3Na$	4	(n-$C_8H_{17}S)_2$	87
5	*iso*-$C_8H_{17}SSO_3Na$	4	(*iso*-$C_8H_{17}S)_2$	87
6	n-$C_7H_{15}SSO_3Na$	4	(n-$C_7H_{15}S)_2$	92
7	n-$C_6H_{13}SSO_3Na$	4	(n-$C_6H_{13}S)_2$	87
8	n-$C_4H_9SSO_3Na$	4	(n-$C_4H_9S)_2$	83
9	$C_6H_5CH_2SSO_3Na$	4	$(C_6H_5CH_2S)_2$	89
10	p-$BrC_6H_4CH_2$-SSO_3Na	4	(p-$BrC_6H_4CH_2S)_2$	90
11	p-$CH_3C_6H_4CH_2$ SSO_3Na	4	(p-$CH_3C_6H_4CH_2S)_2$	86
12	p-$NO_2C_6H_4CH_2$-SSO_3Na	8	(p-$NO_2C_6H_4CH_2S)_2$	88[d]

[a] Reaction conditions: metallic samarium powder (1 mmol), sodium alkyl thiosulfate (1 mmol), water (5 mL) at 90°C.

[b] All reaction products exhibited physical and spectral characteristics in accord with literature values.

[c] Isolated yields.

[d] Methanol (2 mL) was added in the reaction.

The possible mechanism for the formation of disulfides from sodium alkyl thiosulfates promoted by metallic samarium may involve a reduction and homo-coupling reaction process. Sodium alkyl thiosulfate may form an alkyl sulfur free-radical (the reduction process) via single-electron-transfer (SET) in the first step under the reaction conditions, along with cleavage of the sulfur–sulfur bond in the substrate. The alkyl sulfur radical generated then reacts with another alkyl sulfur radical (the coupling process) to afford the symmetrical disulfide in the following step.

In conclusion, we have found that metallic samarium powder is a useful metal for the reduction of sodium alkyl thiosulfates in near boiling water. The remarkable advantages of this reaction are mild, neutral and environmentally friendly reaction conditions, simple operation, and good yields. It may open a new way for using metallic samarium in water without any activating agent in organic synthesis.

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