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Simultaneous Reduction of Nitro Group and S-S Bond in Nitrodisulfides by Samarium Diiodide: A New Approach to Benzothiazolines

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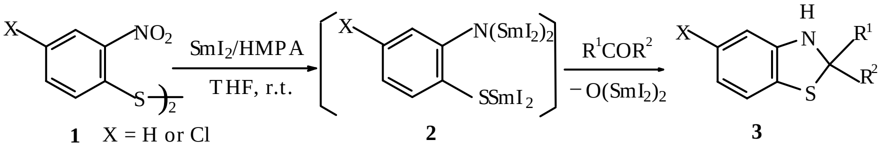
Abstract: Nitrodisulfides were reduced by SmI_2/HMPA in anhydrous THF at room temperature to produce active intermediates (samarium thiolates and amides), which were "living" double-anions and reacted smoothly with aldehydes or ketones to afford benzothiazolines in good yields under mild and neutral conditions.

Keywords: Samarium diiodide, reduction, nitro group, disulfide, benzothiazoline.

As a powerful and versatile one-electron transfer reductant, SmI_2 has been applied widely in organic synthesis[1]. Our previous works on the reduction of nitro compounds and reductive cleavage of S-S, Se-Se, Te-Te bonds with SmI_2[2] led us to investigate the simultaneous reduction of nitro group and S-S bond by SmI_2.

Benzothiazolines derivatives are important reagents and useful intermediates in organic synthesis and pharmaceutical chemistry. For instance, they can be used as addition agents for photographic emulsions[3a], effective acaricides[3b], antituberculous agents[3c], lubricating oil antioxidant[3d], and so on. Several methods had been introduced to prepare this kind of compounds[4]; most of these methods involved in using acid or base catalysts as well as moderate thermal conditions. Here, we described a new approach to benzothiazolines *via* SmI_2 reducing nitro group and S-S bond in nitrodisulfides **1** simultaneously to form intermediates **2** which reacted with aldehydes or ketones smoothly to give benzothiazolines **3** in good yields.(**Scheme 1**)

Scheme 1



1 X = H or Cl **2** **3**

The results are summarized in **Table 1**. When nitrodisulfides **1** were treated with SmI_2/HMPA/THF at room temperature, the reduction of nitro group and reductive cleavage of S-S bond resulted in the formation of trivalent samarium species. According to the relative literatures[5], we considered the trivalent samarium species were the intermediates **2** (samarium thiolates and amides) which were "living" double-anions and reacted smoothly with aldehydes or ketones to afford benzothiazolines **3** in good yields.

In summary, a new approach to benzothiazolines has been elucidated, the advantages of which are readily available starting materials, simple manipulation, mild and neutral conditions.

Table 1 Reaction of nitrodisulfides with aldehydes or ketones by SmI_2[a]

Entry	X	R^1	R^2	T(h)	Yield(%)[b]
3a	H	n-Pr	H	1	87
3b	H	Ph	H	1	85
3c	H	p-$CH_3OC_6H_4$	H	1.5	78
3d	H	Me	Et	2	83
3e	H	Me	Ph	3	68
3f	H	-$(CH_2)_5$-		1	82
3g	Cl	n-Pr	H	1	86
3h	Cl	Ph	H	1	87
3I	Cl	Me	Me	2	88
3j	Cl	Me	Ph	3	65
3k	Cl	-$(CH_2)_4$-		2	79
3l	Cl	-$(CH_2)_5$-		2	80

[a]0.5mmol nitrodisulfides, 1mmol aldehydes or ketones, 7mmol SmI_2 were used; [b]isolated yields based on nitrodisulfides; all products were characterized by IR and ^1H NMR spectra.

General procedure for the benzothiazolines A solution of nitrodisulfides **1** (0.5 mmol) in anhydrous THF (2 ml) were added dropwise to a solution of SmI_2 (7 mmol) and HMPA (1 ml) in THF (30 ml) at room temperature under a dry nitrogen atmosphere. The mixture was stirred for 5 minutes and became yellow gradually. Then aldehydes or ketones (1.2 mmol) in THF (2 ml) were added. After stirred at room temperature for a given time (**Table 1**, the reaction was monitored by TLC), the reaction was quenched with dilute hydrochloric acid (0.1mol/L, 3 ml). The crude product was isolated with usual ways and purified by preparative TLC on silica gel using ethyl acetate and cyclohexane (1: 7) as eluent.

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