Samarium diiodide mediated regeneration of 1,2-benzenediamine and preparation of benzimidazolin-2-ones from 2,1,3-benzothiadiazoles

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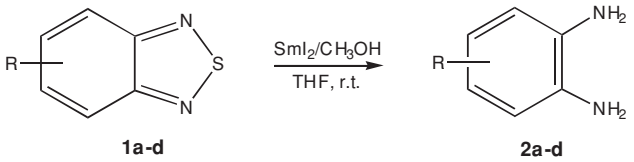
On treatment with SmI_2 in THF and in the presence of methanol, 2,1,3-benzothiadiazoles underwent reductive N–S bond cleavage leading to 1,2-benzenediamines in high yields. Without methanol but in the presence of triphosgene, benzimidazolin-2-ones were obtained in moderate yields under mild conditions.

Keywords: 2,1,3-benzothiadiazoles, benzenediamines, benzimidazolin-2-ones, samarium(II) iodide

The development of procedures for the effective cleavage of the 2,1,3-benzothiadiazole ring to regenerate the diamine functionality is of interest. Several methods for this purpose have been reported. Of the reagents, lithium aluminum hydride[1a] is so strong a reducing reagent that reducible groups (*e.g.* bromo, chloro or cyano) on the aromatic ring may be reduced simultaneously under the reaction conditions. Sodium borohydride[1b] is not reactive enough; only electron deficient 2,1,3-benzothiadiazoles can be reduced with this reagent. Recently, an ecologically clean and efficient method for this purpose has been reported, in which an excess of metallic magnesium together with methanol was used as the reducing reagent.[1c] There is still need for more convenient and practical methods for this transformation.

Samarium(II) iodide (Kagan's reagent) is exceptionally effective in promoting reductive reactions. It has been reported that SmI_2 can cleave the C–S bond in thiocyanates to form disulfides in fair yields.[2] However, to our knowledge there is no literature precedent for the reductive cleavage of N–S bonds in 2,1,3-benzothiadiazoles by this reagent. We here describe an efficient reduction of 2,1,3-benzothiadiazoles with SmI_2 in the presence of methanol to afford 1,2-benzenediamines in good yields (Scheme 1).



1a-d **2a-d**

Scheme 1

Results and discussion

Four different 2,1,3-benzothiadiazoles bearing electron-donating or electron-withdrawing substituents respectively were selected as starting materials. It has been shown that when 2,1,3-benzothiadiazoles 1 were treated with 2 equiv. of SmI_2 at room temperature under a nitrogen atmosphere in the presence of methanol, the deep blue colour of SmI_2 changed to a brown-red colour immediately. The reaction process was monitored by TLC and it showed that the whole process, including the consumption of the starting material and the formation of the desired benzenediamines, was complete within a few minutes. The results are summarised in Table 1.

From Table 1, we can see that 2,1,3-benzothiadiazoles bearing electron donating groups (4-methyl and 4,5-dimethyl, entries 2–3) and 2,1,3-benzothiadiazoles bearing electron withdrawing group (4-Cl, entry 4) underwent reductive cleavage smoothly under similar reaction conditions. The absence of an observable substituent effect and the intactness of reducible groups, such as chloro, suggest that this method may afford a general path for the regeneration of 1,2-benzenediamines from 2,1,3-benzothiadiazoles compared with those involving reagents such as lithium aluminum hydride or sodium borohydride with the limitations mentioned above.[1] Unfortunately, when substrates bearing a highly reducible group, such as nitro or cyano, were treated with SmI_2, the desired products could not be obtained since these reactive groups were reduced by SmI_2 together with the thiadiazole ring.

The mechanism may involve an anionic intermediate resulting from the cleavage of the carbon-nitrogen bonds in **1**, which is then trapped by methanol to afford **2**. Based on this speculation, we felt it worthwhile to try other trapping agents with expectation to get useful products in addition to benzenediamines. Since triphosgene is a very useful carbonyl source in organic synthesis, we investigated the possibility of one-pot preparation of benzimidazolin-2-one derivatives directly from 2,1,3-benzothiadiazoles using triphosgene to trap the intermediate from the reaction of 2,1,3-benzothiadiazoles and SmI_2. We were pleased to find that benzimidazolin-2-ones were successfully obtained (**3**, Scheme 2) in fair yields. The results were listed in Table 1.

Methods for the preparation of the benzimidazolin-2-one skeleton have been extensively studied since many compounds containing this heterocyclic nucleus are of industrial or

Table 1 Regeneration of benzenediamines (**2**) and synthesis of benzimidazolinones (**3**) from 2,1,3-benzothiadiazoles (**1**) promoted by SmI_2

		Synthesis of **2a–d**		Synthesis of **3a–d**	
Entry	Substituent R in **1a–d**	Reaction time /min	Isolated yield of **2** /%	Reaction time /min	Isolated yield of **3** /%
a	H	15	88	90	66
b	5-Me	20	91	120	61
c	5,6-Me_2	20	87	120	62
d	5Cl	15	82	90	57

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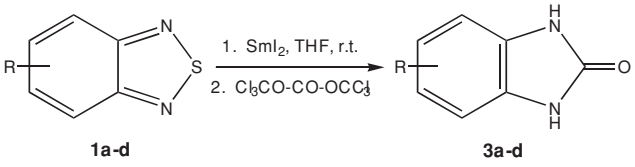

Scheme 2

biological interest.[3] In addition, benzimidazolin-2-ones have been used as intermediates in organic synthesis.[4] Generally, the condensation of a 1,2-diaminobenzene with a carbonyl source such as urea, phosgene or carbon dioxide provides the most direct route to benzimidazolin-2-ones. In practice, this is not always a convenient laboratory conversion because in some cases elevated temperature and pressure are required. In our hands, with the use of SmI_2, benzimidazolin-2-one derivatives can be obtained directly from 2,1,3-benzothiadiazoles and triphosgene in moderate yields under very mild conditions. Therefore the method may be of practical value on a laboratory scale.

In conclusion, with its good yields, short reaction time, mild and neutral conditions, the present work may provide a useful method for the regeneration of 1,2-benzenediamines and the preparation of benzimidazolin-2-ones from 2,1,3-benzothiadiazoles. Further studies to clarify the mechanism of this process and to develop other new uses of 2,1,3-benzothiadiazoles as intermediates in organic synthesis are now in progress in our laboratory.

Experimental

Melting points were obtained on an electrothermal melting point apparatus. Infrared spectra were recorded on a Bruker Vector 22 spectrometer using KBr pellets; absorption maxima are indicated in cm^{-1}. ^1H NMR spectra of $CDCl_3$ solutions were recorded on a Bruker AC–80 spectrometer. Chemical shifts are expressed in ppm downfield from internal tetramethylsilane. Mass spectra were recorded on a HP 5989B MS spectrometer. Tetrahydrofuran (THF) was distilled from sodium-benzophenone immediately prior to use. 2,1,3-Benzothiadiazole derivatives were prepared by known procedures.[5] All reactions were performed in a Schlenk type glass apparatus under a nitrogen atmosphere.

Typical procedure for the regeneration of 4-methyl-1,2-benzenediamine **(2b)**: Under anhydrous conditions, a mixture of powdered samarium (0.30 g, 2 mg-atom) and iodine (0.50 g, 2 mmol) in dry THF (20 ml) was stirred at room temperature until powdered samarium disappeared. To the resulting dark blue suspension of SmI_2 was added methanol (0.5 ml) and 5-methyl-2,1,3-benzothiadiazole (**1b**, 0.15 g, 1 mmol). The mixture was stirred at room temperature for 20 min. At completion, the reaction mixture was poured into H_2O (10 ml) and extracted with diethyl ether (3 × 15 ml). The combined extracts were washed successively with saturated aqueous $Na_2S_2O_3$ (15 ml) and NaCl (15 ml) and dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the crude product was purified by preparative TLC on silica gel using ethyl acetate-cyclohexane (1 : 4) as eluent to yield **2b**.

Other 1,2-benzenediamine derivatives (**2a**, **2c** and **2d**) can be obtained similarly and were fully characterised by their physical data and spectral characteristics. Yields and reaction times are given in Table 1.

2a: m.p. 101–103 °C (lit.[6a] 104 °C). ^1H NMR (80 MHz, $CDCl_3$): δ 6.46–6.54 (m, 2H), 6.32–6.41 (m, 2H), 3.30 (br s, 4H).

2b: m.p. 85–87 °C (lit.[7] 87–89 °C). ^1H NMR (80 MHz, $CDCl_3$): δ 6.51–6.65 (m, 3H), 3.22 (br s, 4H), 2.20 (s, 3H).

2c: m.p. 125–127 °C (lit.[6b] 127–129 °C). ^1H NMR (80 MHz, $CDCl_3$): δ 6.15 (s, 2H), 3.26 (br s, 4H), 2.26 (s, 6H).

2d: m.p. 77–78 °C (lit.[8] 77–78 °C). ^1H NMR (80 MHz, $CDCl_3$): δ 6.21–6.55 (m, 3H), 3.25 (br s, 4H).

Typical procedure for the preparation of 5-methylbenzimidazolin-2-one **(3b)**: To a dark blue suspension of SmI_2 (2 mmol) in THF was added 5-methyl-2,1,3-benzothiadiazole (1b, 0.15 g, 1 mmol). The mixture was stirred at room temperature for 20 min. To the reaction mixture was added triphosgene (0.30g, 1 mmol). Stirring was continued for another hour. At completion, the reaction mixture was poured to H_2O (15 ml) and extracted with ethyl acetate (3 × 15 ml). The combined extracts were washed subsequently with a saturated solution of $Na_2S_2O_3$ (15 ml) and a saturated solution of NaCl (15 ml) and dried over anhydrous Na_2SO_4. After evaporating the solvent under reduced pressure, the crude product was recrystallised from ethanol to give **3b**. Other benzimidazolin-2-one derivatives (**3a**, **3c** and **3d**) were obtained similarly and were fully characterised by their physical data and spectral characteristics. Yields and reaction times are given in Table 1.

3a: m.p. 304–306 °C (lit.[9] 307 °C). IR (KBr) ν: 3439 (NH), 1760 (C=O) cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ: 10.05 (br s, 2H), 6.78–6.89 (m, 2H), 7.34–7.43 (m, 2H). MS: *m*/*z* (%) 134 (M^+, 100).

3b: m.p. 295–297 °C (lit.[7] 299–300 °C). IR (KBr) ν: 3442 (NH), 1757 (C=O) cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ: 10.43 (br s, 2H), 6.70–6.79 (m, 3H), 2.27 (s, 3H); MS: *m*/*z* (%) 148 (M^+, 100).

3c: m.p. >330 °C (lit.[10] >345 °C). IR (KBr) ν: 3441 (NH), 1757 (C=O) cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ: 9.56 (br s, 2H), 7.01 (s, 2H), 2.30 (s, 6H); MS: *m*/*z* (%) 162 (M^+, 100).

3d: m.p. >310 °C (lit.[9] 324–326 °C). IR (KBr) ν: 3450 (NH), 1742 (C=O) cm^{-1}; ^1H NMR (80 MHz, $CDCl_3$) δ: 9.66 (br s, 2H), 6.88–7.23 (m, 3H). MS: *m*/*z* (%) 168 (M^+, 100), 170 (M^+ + 2, 34).

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