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Reductive Cyclization of *o*-Nitrophenylazobenzenes to 2-Aryl-2*H*-benzotriazoles by SmI_2

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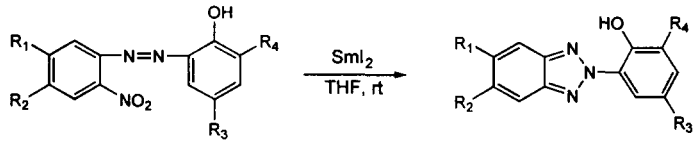
Abstract: In a mild reaction with SmI_2, ortho-nitro substituted phenylazobenzenes have been converted into 2-aryl-2*H*-benzotriazoles. © 1997 Elsevier Science Ltd.

Although samarium diiodide mediated reaction has been developed into a powerful synthetic method during the last decade,[1] there are a limited number of literature precedents for reaction with the nitro functionality.[2-5] Furthermore there are, to our knowledge, no literature examples of the samarium diiodide mediated reductive cyclization of nitro substituted compounds to yield nitrogen containing heterocyclic compound.

2-(2'-Hydroxyphenyl)-2*H*-benzotriazoles (**2**) are widely used as ultraviolet absorbers for the protection of commercially important plastics against sunlight.[6] A wide variety of reagents have been employed for the conversion of *o*-nitrophenylazobenzenes (**1**) to **2**.[7-11] However, most of the methods have limitations, *e.g.* benzotriazole *N*-oxide formation,[8] formation of *o*-aminoazophenols which are hard to remove from the major product,[10] dechlorination of chloro substituted *o*-nitrophenylazo dyes,[11] work-up difficulties,[12] and/or drastic reaction conditions. Moreover, there are no examples of reactions under neutral condition. Herein we describe an efficient and mild reductive cyclization of **1** with SmI_2 in THF, at room temperature, to the corresponding benzotriazoles **2** without the formation of any *o*-aminoazophenols or benzotriazole *N*-oxides (Scheme 1).

Our work concerning the reductive cyclization of **1** using SmI_2 is summarized in the Table. The driving force for such transformations is believed to come from the powerful reducing ability of Sm^{2+} [E^{o} (Sm^{3+}/ Sm^{2+}) = -1.55 V] which behaves as a one-electron donor. The high yields of the cyclized products **2** demonstrate the efficiency of this new method.

Scheme 1



1a ; R_1 = H, R_2 = H, R_3 = *t*-Bu, R_4 = *t*-Bu **2a**

1b ; R_1 = H, R_2 = Cl, R_3 = *t*-Bu, R_4 = *t*-Bu **2b**

1c ; R_1 = H, R_2 = H, R_3 = *t*-pentyl, R_4 = *t*-pentyl **2c**

1d ; R_1 = H, R_2 = H, R_3 = Me, R_4 = H **2d**

1e ; R_1 = Cl, R_2 = H, R_3 = *t*-Bu, R_4 = *t*-Bu **2e**

Benzotriazole *N*-oxide was observed if less than ~ 6 equiv. of SmI_2 was used (Table, entries 1, 2). With increasing amounts of SmI_2, the benzotriazole *N*-oxide decreased gradually [4 equiv. of SmI_2, 10% (Table, entry 1); 5 equiv. of SmI_2, 3% (Table, entry 2)] and none of the intermediate benzotriazole *N*-oxide was observed if more than 6 equiv. of SmI_2 was used. Apparently the reductive cyclization of **1** to **2** proceeds through an intermediate stage involving the benzotriazole *N*-oxide.[13] The optimum condition for the reductive cyclization was obtained by using 7 equiv. of SmI_2 at room temperature (Table, entries 6 - 10). It is worth mentioning that chloro-substituted *o*-nitrophenylazobenzenes **1b** or **1e** reacted without giving any of dechlorinated products even though SmI_2 has a quite powerful electron donating ability. If we added protic

Table. Reductive Cyclization of *o*-Nitrophenylazobenzenes (**1**) using SmI_2 in THF.[a]

entry	substrate	SmI_2	conditions	product	yield (%)
1	**1a**	4 equiv.	rt, 4 h.	**2a**	34[b,c]
2	**1a**	5 equiv.	rt, 4 h.	**2a**	43[b,d]
3	**1a**	6 equiv.	rt, 2.5 h.	**2a**	70[e]
4	**1a**	7 equiv.	MeOH (5 mL)[f], rt, 2.5 h.	**2a**	28[e,g]
5	**1a**	7 equiv.	HMPA (2 mL)[h], rt, 2.5 h.	**2a**	25[e,i]
6	**1a**	7 equiv.	rt, 2.5 h.	**2a**	94[e]
7	**1b**	7 equiv.	rt, 2.7 h.	**2b**	84[e]
8	**1c**	7 equiv.	rt, 2.7 h.	**2c**	85[e]
9	**1d**	7 equiv.	rt, 50 min.	**2d**	97[e]
10	**1e**	7 equiv.	rt, 40 min.	**2e**	91[e]

[a]All reactions were carried out with 0.3 mmol of reactant (**1**) in 20 mL of THF. [b]Isolated yield. [c]10% of benzotriazole *N*-oxide was obtained and 22% of **1a** was recovered. [d]3% of benzotriazole *N*-oxide was obtained and 20% of **1a** was recovered. [e]GC yield with an internal standard, *n*-decane. [f]15 mL of THF was used. [g]35% of **1a** was recovered. [h]18 mL of THF was used. [i]43% of **1a** was recovered.

solvents such as MeOH or polar solvents such as HMPA to the reaction mixture, mixtures of several products including **1a** and **2a** were formed and the yield of **2a** was not as good as the reaction in THF (Table, entries 4, 5).

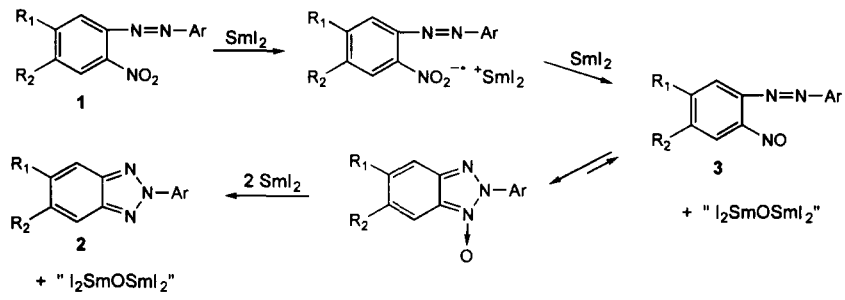
A typical procedure for the SmI_2 mediated cyclization reaction follows. To a stirred solution of freshly prepared SmI_2 (from Sm/CH_2I_2) in THF (10 mL) under the nitrogen atmosphere was added a solution of the *o*-nitrophenylazobenzene **1** (0.3 mmol) in THF (10 mL) dropwise using a syringe pump (15 - 20 min.) at room temperature. The reaction mixture was stirred at room temperature until the reaction was complete, and poured into a solution of 10% aqueous NH_4Cl. The mixture was extracted with diethyl ether (3 x 30 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated. The residue was chromatographed over silica gel (hexane /EtOAc, 99 : 1) to give **2**.

To confirm the intermediacy of benzotriazole *N*-oxide formation, electrolysis reactions were carried out. Based on the cyclic voltametric behavior, **1a** was reduced under a controlled potential [Pt cathode and anode, 0.4 M $LiClO_4$/(MeOH : CH_2Cl_2 = 1 : 1, v/v), - 0.75 V vs. Ag/AgCl] using a devided H cell. As we expected, benzotriazole *N*-oxide was obtained exclusively in 93% yield without the formation of **2a**. By changing the conditions of the electrolysis [Pt cathode and anode, 0.2 M NaOH/(THF : H_2O = 1 : 1, v/v), - 1.3 V vs. Ag/AgCl], **1b** or the *N*-oxide derived from **1b** is transformed to **2b** as the exclusive product in 92% (starting substrate; **1b**) and 97% (starting substrate; *N*-oxide derived from **1b**). It is apparent that the electron transfer ability controls the reductive cyclization reaction.

Little mechanistic information is currently available for the reactions of nitrogen compounds with SmI_2. Evans reported that 2 equiv. of $Sm(C_5Me_5)_2$ deoxygenated pyridine *N*-oxides or 1,2-epoxybutane and was transformed into the complex $(C_5Me_5)_2Sm\text{-}O\text{-}(C_5Me_5)_2$ whose structure was established by X-ray crystallography.[14] Zhang and Lin also demonstrated the deoxygenation of pyridine *N*-oxides by SmI_2.[4] By analogy, when SmI_2 is either used to cyclize *o*-nitrophenylazobenzenes (**1**) by transferring electrons to nitro group or used to remove an oxygen atom from *N*-oxide, the formation of a complex $I_2Sm\text{-}O\text{-}SmI_2$ can be postulated. This species may later disproportionates into SmI_3 and a soluble species "SmIO" whose exact structure is not established yet. Based on Evans' and our results, a possible reaction mechanism is shown in Scheme 2. The unstable intermediates, *o*-nitrosophenylazobenzenes (**3**) may immediately form the benzotriazole *N*-oxides. Further controlled experiments are currently under way to prove pathways of the reaction mechanism in detail.

In summary, the reductive cyclization of aromatic nitro compounds using SmI_2, provides an efficient and selective method for the synthesis of 2-(2'-hydroxyphenyl)-2*H*-benzotriazoles which are commercially useful ultraviolet absorbers.

Scheme 2



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References and Notes

1. Molander, G. A.; Harris, C. R. *Chem. Rev.* **1996**, *96*, 307.
2. Souppe, J.; Danon, L.; Namy, J. L.; Kagan, H. B. *J. Organometal. Chem.* **1983**, *250*, 227.
3. Kagan, H. B.; Namy, J. L.; *Tetrahedron* **1986**, *42*, 6573.
4. Zhang, Y.; Lin, R. *Synth. Commun.* **1987**, *17*, 329.
5. Sturgess, M. A.; Yarberry, D. J. *Tetrahedron Lett.* **1993**, *34*, 4743.
6. Gachter, R.; Muller, H. *Plastics Additives Handbook*,. 3rd ed.; Hanser Publisher: New York, 1990; p25.
7. Rosevear, J.; Wilshire, J. *Aust. J. Chem.*. **1984**, *37*, 2489.
8. Rosevear, J.; Wilshire, J. *Aust. J. Chem.*. **1982**, *35*, 2089.
9. White, H. L.; Krolewski, C. V. Ger. Pat. 2620896, 1976; *Chem. Abstr.* **1977**, *86*, 106598s.
10. Ziegler, C. E.; Peterli, H. J. Swiss Pat. 615165, 1980; *Chem. Abstr.* **1980**, *93*, 8181a.
11. White, H. L.; Ger. Pat. 2551853, 1976; *Chem. Abstr.* **1976**, *85*, 108646j.
12. Baik, W.; Park, T. H.; Kim, B. H.; Jun, Y. M. *J. Org. Chem.* **1995**, *60*, 5683.
13. Electrochemically prepared benzotriazole *N*-oxide derived from **1a** was transformed to **2a** exclusively (>98%) within 10 min. by the SmI_2 reduction at room temperature.
14. Evans, W. J.; Grate, J. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 405.

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