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Efficient Reduction of Aryl Azides and Aryl Nitro Compounds to Their Corresponding Amines with Sulfurated Calcium Borohydride CA(BH<sub>2</sub>S<sub>3</sub>)<sub>2</sub>. A New Modified Borohydride Agent H. Firouzabadi<sup>a</sup>, B. Tamami<sup>a</sup> & A. R. Kiasat<sup>a</sup>

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### EFFICIENT REDUCTION OF ARYL AZIDES AND ARYL NITRO COMPOUNDS TO THEIR CORRESPONDING AMINES WITH SULFURATED CALCIUM BOROHYDRIDE CA(BH<sub>2</sub>S<sub>3</sub>)<sub>2</sub>. A NEW MODIFIED BOROHYDRIDE AGENT.

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**ABSTRACT:**  $Ca(BH_2S_3)_2$  is easily prepared by metathetical reaction between NaBH<sub>2</sub>S<sub>3</sub> and CaCl<sub>2</sub> in THF. Ca(BH<sub>2</sub>S<sub>3</sub>)<sub>2</sub> is much more stable than NaBH<sub>2</sub>S<sub>3</sub> therefore, is a more practical reagent. Sulfurated calcium borohydride can easily reduce aryl nitro and aryl azido functions to their amines in high yields in refluxing THF. Reduction of nitro groups is accompanied with regioselectivity. Very high chemoselectivity is also observed for the reduction of an azido functional group in the presence of nitro functionality.

During the past decades, NaBH<sub>4</sub> has been always playing an important role in modern organic synthesis<sup>1</sup>. Unfortunately, this compound does not usually convert aryl azides and aryl nitro derivatives to the corresponding aniline compounds in good yields.<sup>2,3</sup> Number of methods describing reduction of azides by different reagents are reported in the literature<sup>4,5</sup>. Some disadvantages in relation to the selectivity, general applicability have been observed with the

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LiAH<sub>4</sub> and NaBH<sub>4</sub> for this purpose. For instance, LiAlH<sub>4</sub> is not tolerable to many functionalities such as  $CO_2R$ ,  $NO_2$  etc. and NaBH<sub>4</sub> normally gives poor yields in the conversion of azides to amines<sup>5</sup>

Reduction of nitro compounds to primary amines under mild conditions and in the absence of protic solvents is of practical importance. With LiAlH<sub>4</sub> aromatic nitro compounds leads mainly to azo derivatives and also many other functional groups are reduced at the same time<sup>6</sup>. However, it was also reported that aromatic nitro compounds afforded azoxy, azo, and primary amines on heating directly with NaBH<sub>4</sub><sup>7</sup>. Thus, a simple and efficient reducing agent of general applicability for the reduction of aryl azides and aryl nitro compounds will be well appreciated.

It has been previously demonstrated that treatment of NaBH<sub>4</sub> with a proper amount of S<sub>8</sub> in anhydrous THF under mild experimental conditions produces sodium sulfurated borohydride, NaBH<sub>2</sub>S<sub>3</sub> with the proposed structures as indicated in Scheme 1. A broad coverage of usage of this reducing agent is available in the literature.<sup>6,8</sup> The instability of the reagent which decomposes rapidly in the presence of oxygen or atmospheric moisture puts limitation upon its uses as a practical reducing agent. Search in the literature revealed that there is no report on preparation and use of the modified form of this reagent in order to overcome the existing problems.

$$Na^{+} H \xrightarrow{S} S \xrightarrow{S^{-}} \Rightarrow Na^{+} \begin{bmatrix} H \xrightarrow{S} S \\ H \xrightarrow{S} S \end{bmatrix} \Rightarrow 2Na^{+} \begin{bmatrix} H \xrightarrow{S-S-S} H \\ H \xrightarrow{S-S-S} \end{bmatrix}$$

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In continuation of our interest for preparation and application of new modified borohydrides<sup>9,10</sup>, we now wish to report the preparation of  $Ca(BH_2S_3)_2$  and explore the applications as of this compound for the reduction of varieties of functional groups.

 $NaBH_2S_3$  was prepared according to the reported procedure (eq 1)<sup>8</sup> which was subsequently used for the preparation of  $Ca(BH_2S_3)_2$  by metathetical reaction with  $CaCl_2$  in THF(eq 2).

NaBH<sub>4</sub> + 3S 
$$\longrightarrow$$
 NaBH<sub>2</sub>S<sub>3</sub> + H<sub>2</sub> (eq 1)  
2NaBH<sub>2</sub>S<sub>3</sub> + CaCl<sub>2</sub>  $\longrightarrow$  Ca(BH<sub>2</sub>S<sub>3</sub>)<sub>2</sub> + 2NaCl (eq 2)

The effect of metal cation exchange on the stability of the sulfurated borohydride has been determined by the acidic hydrolysis and estimated by the amount of hydrogen evolved during the hydrolytic reaction in different time intervals for portions of 0.1 g of the compound. By comparison of the results, it is concluded that the stability of  $Ca(BH_2S_3)_2$  is much more than that shown by NaBH<sub>2</sub>S<sub>3</sub>.

Now, in this study we report that  $Ca(BH_2S_3)_2$  in THF is able to reduce azides easily to their corresponding amines in good to excellent yields (Table 1). The nature and the position of the substituted groups do not influence the rate and the yields of the products. By this method absolute selectivity is observed for the reduction of -N<sub>3</sub> functionality in presence of -NO<sub>2</sub> group (entry 6, Table 1).

The reduction of nitroarenes with the presented reducing agent in THF under reflux conditions proceeded smoothly and afforded the corresponding amines in good to excellent yields (Table 1). The nature of the substituents does not affect the rates and the yields of the reduction drastically.

Entry	Substrate	Produ Ti	me (h)	Yield	m.p or b.p (°C) <sup>12</sup>
1	()-N <sub>3</sub>		1	91	183
2			3	87	198
3			2.1	86	204
4	CH <sub>3</sub>	CH <sub>3</sub> -NH <sub>2</sub>	0.8	90	49.5-52
5			0.8	84	87-90
6	02N-0-N3		0.7	86	147-148.5
7			2.5	90	183
8		H <sub>2</sub> N-O-NH <sub>2</sub>	6.9	88	140-142
9			12	82	201-202.5
10			7.2	89	185-187
11			6	84	227-228.5
12			3.5	90	69-71
13			4.5	88	185-187
14			12	89	51

Table 1 : Reduction of Azides and Nitro Compounds to Their Corresponding Aminesin THF Under Reflux Conditions.

Entry	Substrate	Product	Time (h)	Yield
1			12	72 15
2			12	63
	°CH <sub>3</sub>	`CH₃		20
3		NH <sub>2</sub> NH <sub>2</sub>	12	80
				10

Table 2: The Effect of Steric Hindrance Upon the Rate of Reduction of  $-NO_2$  Groups by  $Ca(BH_2S_3)_2$  in THF

In order to appreciate the relative importance of the steric effect, upon the rate of reduction, various pairs of nitro substituted aryl compounds were reduced together. The results show that more hindered  $-NO_2$  group is more difficult to be reduced. These results are shown in Table 2. Some of the results of this investigation have been compared with some of those reported by NaBH<sub>2</sub>S<sub>3</sub> for the reduction of aromatic nitro compounds<sup>6</sup> in Table 3. We have also compared

Entry	Substrate	NaBH <sub>2</sub> S <sub>3</sub> ratio / time(h) / yield			Ca(BH <sub>2</sub> S <sub>3</sub> ) <sub>2</sub> ratio / time(h) / yield		
1	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub>	2:1	24	95	2:1	2.5	90
2		1:1	24	49	2:1	12	89
3	m-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	1:1	24	80	2:1	8.5	87
4	P-CIC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	1:1	24	79	2:1	3.5	90

Table 3: Comparison of Reducing Ability of Ca(BH<sub>2</sub>S<sub>3</sub>)<sub>2</sub> with NaBH<sub>2</sub>S<sub>3</sub>

some of the results of the reduction of aromatic azido compounds by  $Ca(BH_2S_3)_2$ with some other reagents<sup>4,5,11</sup> in Table 4.

#### **CONCLUSION:**

In this study, we have introduced a new modified borohydride agent which is able to reduce nitro and azide functional groups easily with high yields. We have observed that  $Ca(BH_2S_3)_2$  is much more stable than  $NaBH_2S_3$ .  $Ca(BH_2S_3)_2$ shows a good selectivity for the reduction of azide groups in the presence of nitro functionality. This reagent is also able to show regioselectivity for the reduction of nitro groups in nitro aryl compounds.

Preparation of  $Ba(BH_2S_3)_2$  and  $Sr(BH_2S_3)_2$  and their applications are underway in our laboratories.

Entry	Substrate	Ca(BH <sub>2</sub> S <sub>3</sub> ) <sub>2</sub> time(h) / yield		$Zn(BH_4)_2^a$ time(h) / yield		Zn(BH <sub>2</sub> ) <sub>2</sub> /dabco time(h) / yield		Zn-NiCl <sub>2</sub> , 6H <sub>2</sub> O time(h) / yield	
1	C <sub>6</sub> H <sub>5</sub> N <sub>3</sub>	1	91	1.5	70	-	•	24	90
2	P-NO2C6H4N3	0.7	86	1.5	90	0.85	97	2.5	80
3	PÆtO <sub>2</sub> C-C <sub>6</sub> H <sub>4</sub> N <sub>3</sub>	0.8	84	-	-	7.3	92	2	80
4	m-CNC <sub>6</sub> H <sub>4</sub> N <sub>3</sub>	0.8	90	-	-	2.4	94	-	-

Table 4: Comparison of  $Ca(BH_2S_3)_2$  With  $Zn(BH_4)_2^{11}$ ,  $Zn(BH_4)_2$ .dabco<sup>4</sup>, and Zn-NiCl<sub>2</sub>.6H<sub>2</sub>O<sup>5</sup> for the Reductive Conversion of Azides.

a. The reaction has been carried out under sonication

#### EXPERIMENTAL

#### Preparation of Calcium Sulfurated Borohydride.

Sodium borohydride (3.78 g, 0.1 mol) and sulfur (9.6 g, 0.3 mol) was thoroughly mixed under nitrogen atmosphere in a three-necked flask (250 ml) bearing a condenser and a dropping funnel containing anhydrous THF (50 ml). THF was rapidly added to the dry solid mixture, upon which a brisk exothermic reaction with evolution of hydrogen gas ensues. The flask being kept cool in an ice water bath and under N<sub>2</sub> atmosphere. After the initial reaction had subsided (~15 min), stirring at 25°C was continued for another 30 min. To the resulting suspension, freshly fused CaCl<sub>2</sub> (5.55 g, 0.05 mol) was added. The reaction mixture was magnetically stirred for 24 h at room temperature and subsequently by careful evaporation of the solvent under vacuum resulted Ca(BH<sub>2</sub>S<sub>3</sub>)<sub>2</sub> in a quantitative yield.

# Reduction of Phenyl Azide to Aniline with $Ca(BH_2S_3)_2$ . A Typical Procedure for the Reduction of Azides.

Phenyl azide (0.12 g, 1 mmol) in THF (5ml) was added to the suspension of Ca(BH<sub>2</sub>S<sub>3</sub>)<sub>2</sub> (0.57g, 1.5 mmol) in dry THF (10 ml) and the mixture was stirred under reflux conditions for 1 h. Progress of the reaction was monitored by TLC. After completion of the reaction, the solvent was evaporated under reduced pressure at room temperature. The residual solid was hydrolyzed with a HCl solution (10%) in the Et<sub>2</sub>O (15 ml) until the pH of the reaction mixture reaches 1. The precipitated sulfur was filtered off and the filtrate was washed repeatedly with Et<sub>2</sub>O (15 ml). The aqueous layer was separated and the pH of the mixture adjusted about 11 with a solution of NaOH (10%). The aqueous layer was extracted again with Et<sub>2</sub>O (15 ml) and the combined extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated to result aniline in 91% yield.

## Reduction of Nirobenzene to Aniline with $Ca(BH_2S_3)_2$ . A Typical Procedure for the Reduction of Nitro Compounds.

In a round bottomed flask (25 ml) equipped with a magnetic stirrer, a suspension of  $Ca(BH_2S_3)_2$  (0.75g, 2 mmol) in anhydrous THF (10 ml) was prepared. Nitrobenzene (0.123 g, 1 mmol) in THF (5 ml) was added dropwise and the reaction mixture was stirred under reflux conditions for 2.5 h. After completion of the reaction (monitored by TLC), the solvent was evaporated under reduced pressure at room temperature. The residual solid was hydrolyzed with a HCl solution (10%) in the Et<sub>2</sub>O (15 ml) until the pH of the reaction mixture

reaches 1. The precipitated sulfur was filtered off and the filtrate was washed repeatedly with  $Et_2O$  (15 ml). The aqueous layer was separated and the pH of the mixture adjusted about 11 with a solution of NaOH (10%). The aqueous layer was extracted again with  $Et_2O$  (15 ml) and the combined extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated to result aniline in 90% yield.

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