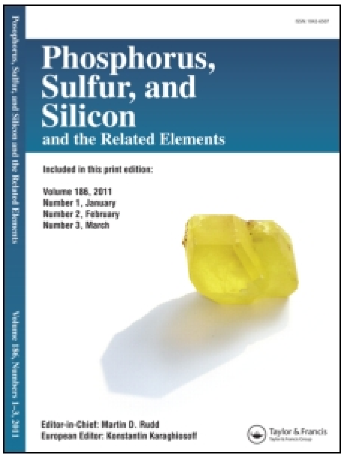

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

A NEW STABLE MODIFIED BOROHYDRIDE REAGENT, EFFICIENT REDUCTION OF DIFFERENT FUNCTIONAL GROUPS WITH SULFURATED BARIUM BOROHYDRIDE [BA(BH$_2$S$_3$)$_2$] IN DRY THF

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To cite this Article Firouzabadi, Habib and Ghadami, Mahboobeh(2000) 'A NEW STABLE MODIFIED BOROHYDRIDE REAGENT, EFFICIENT REDUCTION OF DIFFERENT FUNCTIONAL GROUPS WITH SULFURATED BARIUM BOROHYDRIDE [BA(BH$_2$S$_3$)$_2$] IN DRY THF', Phosphorus, Sulfur, and Silicon and the Related Elements, 166: 1, 83 — 98
To link to this Article: DOI: 10.1080/10426500008076533
URL: http://dx.doi.org/10.1080/10426500008076533

Phosphorus, Sulfur and Silicon, 2000, Vol. 166, pp. 83-98
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A NEW STABLE MODIFIED BOROHYDRIDE REAGENT. EFFICIENT REDUCTION OF DIFFERENT FUNCTIONAL GROUPS WITH SULFURATED BARIUM BOROHYDRIDE [$BA(BH_2S_3)_2$] IN DRY THF

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(Received April 4, 2000; In final form June 6, 2000)

Barium and strontium sulfurated borohydrides, $Ba(BH_2S_3)_2$.$Sr(BH_2S_3)_2$ the two newly introduced modified borohydride agents, are prepared from $NaBH_2S_3$ by metathesis reaction with $BaCl_2$ and $SrCl_2$ in good yields. $Ba(BH_2S_3)_2$ is more stable and more reactive than $Sr(BH_2S_3)_2$.The reducing ability of $Ba(BH_2S_3)_2$ for the reduction of aldehydes, ketones, α,β-unsaturated carbonyl compounds, azides, nitro compounds, and cleavage of epoxides in dry THF is described.

Keywords: Modified borohydride agents; Reduction; Barium sulfurated borohydride; Strontium sulfurated borohydride

INTRODUCTION

Zinc, iron and hydrogen sulfide are among the oldest reducing agents having been used since the forties of the last century[1]. Catalytic hydroganation[2] by Paul Sabatier in 1912 and reduction with metal hydrides[3], especially sodium borohydride in 1943 by the research group headed by H.I. Schlesinger and including H.C. Brown, brought about a revolutionary change in the methodology for the reduction of functional groups in organic molecules.

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Catalytic hydrogenation and metal hydride reduction account for about one fourth of all reductions, the remaining half of the reductions being due to electroreductions and reductions with metals, metal salts and inorganic as well as organic compounds[2]. The inability of selective reduction of carbonyl function of acids, amides, esters, ketones in the presence of carbon double bonds by catalytic hydrogenation has led to the widespread use of certain complex metal hydrides for the reduction of carbonyl groups. Metal hydrides encompass a wide variety of reducing agents which may be used for selective reduction of functional groups in polyfunctional molecules[2b]. These reducing agents include not only the nucleophilic reagents, which reduce polar multiple bonds such as carbonyl groups, but also electrophilic reagents which react readily with nonpolar carbon-carbon multiple bonds.

Sodium borohydride and lithium aluminum hydride are the commonly used hydride transfer agents which provide simple and convenient routes for the reduction of many organic functional groups and they are invariably used in the laboratory for organic synthesis.[1,4] However, in spite of their great convenience, they suffer from certain limitations. Lithium aluminum hydride is an exceedingly powerful reducing agent capable of reducing practically all organic functional groups. Consequently, it is quite difficult to apply it for the selective reduction of multifunctional molecules.[4] On the other hand, sodium borohydride is a remarkably mild reducing agent, and is consequently primarily useful for the selective reduction of a few organic functional groups, such as aldehydes, ketones, acid chlorides, etc[1]. These reagents represent the two extremes of a possible broad spectrum. This situation makes it desirable to develop means of controlling the reducing power of such reagents and such a control could be achieved either by decreasing the reducing power of lithium aluminum hydride or by increasing that of sodium borohydride. In fact, the reducing power of the hydrides can be modified by: a) substitution of the hydride(s) with other groups which may exert marked steric and electronic influences upon the reactivity of the substituted complex ion, b) variation in the alkali metal cation and metal cation in the complex hydride which would alter the reducing power, c) by concurrent cation and hydride exchange, d) use of the ligands to alter behavior of the metal hydrides, e) combination of borohydrides with metals, metal salts, Lewis acids, mixed-solvents, and some other agents, f) changing the cation to quaternary ammonium borohydride, and g) finally use of the polymers to support the hydride species.

Preparation of modified borohydride reagents and their uses in organic synthesis has been reviewed recently[5]. Along the lines of strategies just outlined, numerous modified borohydride reagents have been made over the years in our laboratories and used for reduction of different organic compounds under different reaction conditions[6].

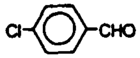
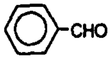
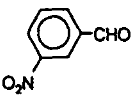
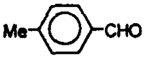
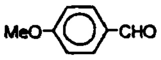
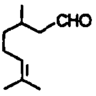
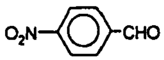
Sodium sulfurated borohydride; $NaBH_2S_3$, which is a white or a yellowish powder, is prepared by the addition of elemental sulfur to sodium borohydride in THF in an ice-water bath under N_2 atmosphere in a quantitative yield [7]: This compound is reasonably stable at room temperature, if kept in a dry nitrogen atmosphere, but decomposes rapidly in the presence of oxygen or atmospheric moisture. This puts restriction on its uses as a practical reducing agent.

Recently, we have reported that sulfurated calcium borohydride is much more stable than its sodium, magnesium, and beryllium analogues and also shows more reactivity than Na, Mg, and its Be analogue for the reduction of substrates under our studies[8]. Now in this report we present the preparation of barium and strontium sulfurated borohydrides; $Ba(BH_2S_3)_2$, $Sr(BH_2S_3)_2$. Barium sulfurated borohydride is more stable than $Ca(BH_2S_3)_2$ and $Sr(BH_2S_3)_2$ and also shows more reactivity for the reduction of different substrates. Some applications of $Ba(BH_2S_3)_2$ for the reductive transformation of functional groups are presented in this article.

RESULTS AND DISCUSSION

Barium and strontium sulfurated borohydrides are prepared under argon atmosphere in dry THF in an ice water bath by the addition of sulfurated sodium borohydride[8] to barium and strontium chlorides. The resulting borohydrides are solid powders with yellowish tone in good yields. The color of the compounds fades away while being stored in a capped bottle. The rate of the color change depends on the exposure of the compounds to the moisture, air and also to the nature of the cation attached to the borohydride moiety. The borohydrides, in this study, were hardly soluble in dry Et_2O, CH_2Cl_2, THF, $CHCl_3$, CCl_4, and petroleum benzene The compounds are unstable in HMPA, ethanol, methanol, and H_2O and are decomposed with a brisk evolution of an odorous gas. The compounds are also sensitive to high temperatures and are decomposed above 150°C.

TABLE I Reduction of aldehydes with an equimolar amount of $Ba(BH_2S_3)_2$ in THF

Entry	*Substance*	*Temp.*	*Time (h)*	*Yield %*
1		rt	2	92
2		rt	1	98
3		rt	2	95
4		-[a]	0.4	89
5		-[a]	0.5	85
6		rt	1	94
7		rt	0.15	90

a. The reaction was performed under reflux conditions.

We have investigated the effect of cations upon the stability of the sulfurated borohydrides in this study. For this purpose, the amount of H_2 gas evolved in hydrolysis of the borohydrides by HCl solution (2N) was measured for 30 days. The results show that Ba $(BH_2S_3)_2$ is more stable than $Sr(BH_2S_3)_2$. The charge density of the cations may be one of the factors that affects the stability and reactivity of the hydrides. Therefore, in this report we have focused our attention to $Ba(BH_2S_3)_2$ which is a more stable and also a more reactive reagent.

For the selection of the appropriate solvent, reduction of 4-methylbenzaldehyde was studied in dry THF, *tert*-butanol, *iso*-propanol, Et_2O, and

CH_2Cl_2. Our observation shows that the reaction in THF was faster and cleaner than in the other solvents under our studies. The required molar ratios of the reagent towards substrates varies with the nature of the substrate. For conversion of aldehydes and ketones to their alcohols, azides to their amines, epoxides to their disulfides one equimolar of the reducer is sufficient and for the reduction of nitro compounds to their amines, 1.5 equimolar of the reagent is required.

REDUCTION OF ALDEHYDES

Reduction of aldehydes to the corresponding primary alcohols (Table I) is performed very efficiently with $Ba(BH_2S_3)_2$. Aromatic aldehydes substituted with electron-withdrawing groups are generally reduced faster than those substituted with electron-releasing groups at either room temperature or under reflux conditions.

Reduction of α,β- unsaturated aldehydes proceeded without any regio-selectivity and saturated alcohols are obtained in high yields.

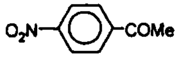
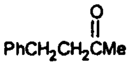
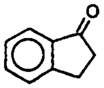
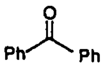
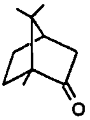
Employing dilute mineral acids, H_2O, or dilute NaOH solutions may effect the work-up of the reaction mixture. In order to minimize the product contamination by elemental sulfur, aqueous solution of NaOH (5%) is recommended. If basic condition had to be avoided, H_2O or dilute mineral acids are employed. The small amount of sulfur that is generally found in the organic phase could be eliminated by filetration after concentration of the reaction mixture.

REDUCTION OF KETONES

Reduction of ketones to their alcohols is performed well in dry THF under reflux conditions. The bulky nature of the reagent induces special steric selectivity for the reduction of sterically hindered carbonyl groups *vs* non-hindered ones. (Table II).

Reduction of α,β-unsaturated ketones are also examined (Table III). Benzalacetone, after reduction, is converted to benzylacetone, which shows that 1,4-reduction has occurred. Therefore, in contrast to the reduction of α,β-unsaturated aldehydes, reduction of α,β-unsaturated ketones is accompanied with regio- selectivity. Generally, this reagent is not reactive enough to be suitable for the reduction of sterically hindered ketones (Table III). The work-up of the reaction mixture is similar to aldehydes, which has been discussed in the preceding section.

TABLE II Reduction of ketones with an equimolar amount of $Ba(BH_2S_3)_2$ in THF under reflux conditions

Entry	*Substance*	*Time (h)*	*Yield %*
1		0.4	90
2	 $\mathrm{PhCH_2CH_2}\overset{\overset{O}{\parallel}}{\mathrm{C}}\mathrm{Me}$	3.6	95
3		24	15
4		24	N. R
5		24	N. R
6	PhCOMe [a]	3	80

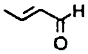
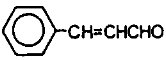
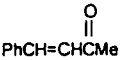
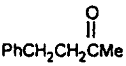
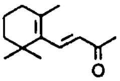
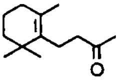
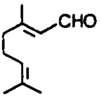
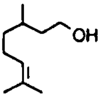
[a] The reaction was performed with 3:1 mole ratio (red/sub).

REDUCTION OF AZIDES

The transformation of azides to amines is a synthetically important process, especially in carbohydrate and nucleoside chemistry[9] and its value has been well stablished[10]. However, some of the reported methods are not chemoselective and /or a drastic reaction condition is required. Reduction of azides with $NaBH_4$ usually give poor yields, except for the reduction of azidobenzene[9]. $NaBH_4$ in the presence of phase-transfer caralysts reduces azides to amines in high yields[11].

$Ba(BH_2S_3)_2$ reduces azides efficiently to the corresponding primary amines in THF at room temperature in high yields (Table IV). α,β-Unsaturated azides are converted to the corresponding α,β-unsaturated amines, which shows regio- and chemoselectivity of the reagent for this purpose.

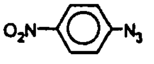
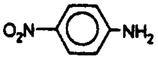
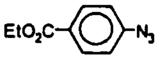
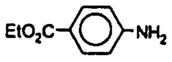
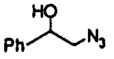
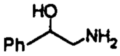
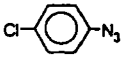
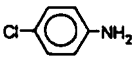
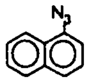
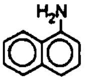
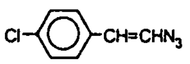
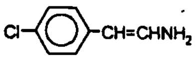
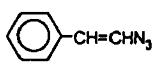
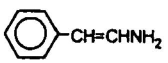
TABLE III Reduction of α,β-unsaturated carbonyl compounds with an equimolar amount of $Ba(BH_2S_3)_2$ in THF at room temperature

Entry	*Substance*	*Time (h)*	*Yield %*	*Product*
1		4	98	$CH_3(CH_2)_3OH$
2		0.3	95	$Ph(CH_2)_3OH$
3	 $PhCH=CH\overset{O}{\overset{\Vert}{C}}Me$	3	85	 $PhCH_2CH_2\overset{O}{\overset{\Vert}{C}}Me$
4		24	trace	
5		2.5	90	

REDUCTION OF AROMATIC NITRO COMPOUNDS

Reduction of aromatic nitro compounds to primary amines is performed in dry THF at reflux with 1.5 molar ratio of the borohydride. α,β-Unsaturated nitro compounds are reduced at room temperature with 1 molar ratio of the reducing agent to α,β-unsaturated amino compounds (Table V). The yields and the rates of the reductions are generally superior to those reported by the other methods[10]. Portion-wise addition of the reducing agent increases the yields of the reductions.

TABLE IV Reduction of azides with an equimolar amount of $Ba(BH_2S_3)_2$ in THF at room temperature

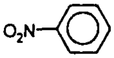
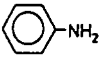
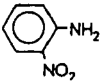
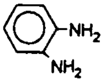
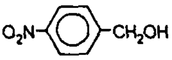
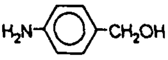
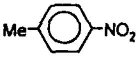
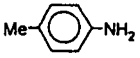
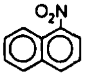
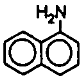
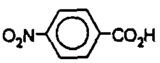
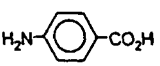
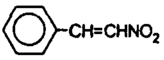
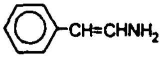
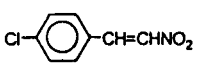
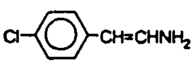
Entry	*Substance*	*Time (h)*	*Yield %*	*Product*
1		–[a]	90	
2		–[a]	95	
3		(2)	85	
4		–[a]	89	
5		(1)	93	
6		–[a]	87	
7		–[a]	88	

a. The reactions occurred spontaneously.

CLEAVAGE OF EPOXIDES

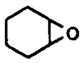
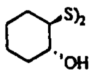
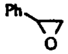
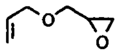
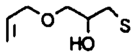
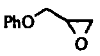
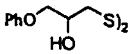
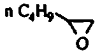
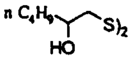
Epoxides are normally cleaved by reaction with alkali metal hydrides to give the corresponding alcohols. The reaction of Ba $(BH_2S_3)_2$ with epoxides is performed in dry THF at room temperature with 1 molar ratio of the reagent. This reaction gives symmetrical bis-(2-hydroxyethyl) disulfides that means the sulfide chain is more available than the hydride ion in the reagent. The stereochemistry of the reaction is similar to the attack of H_2S on the epoxide rings in basic solution. Substituted epoxides are opened from the less hindered side of the ring and the reaction proceeds with good yields (Table VI).

TABLE V Reduction of nitro compounds with 1- 1.5 molar ratio of $Ba(BH_2S_3)_2$ in refluxing THF

Entry	*Substance*	*Time (h)*	*Yield*	*% Product*
1		1.3	98	
2		2	85	
3		1.75	85	
4		3.75	89	
5		1.5	85	
6		2	80	
7		2	90-[a]	
8		2	95-[a]	

a. The reaction was performed at room temperature with 1 equimolar of the reagent.

TABLE VI Reaction of epoxides with an equimolar amount of $Ba(BH_2S_3)_2$ in THF at room temperature

Entry	*Substance*	*Time (min)*	*Yield %*	*Product*
1		10	90	
2		30	97	$PhCH(OH)CH_2S]_2$
3		20	89	
4		20	96	
5		20	92	

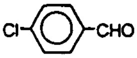
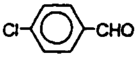
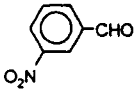
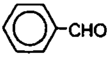
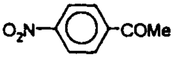
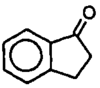
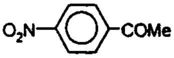
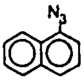
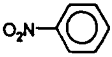
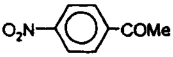
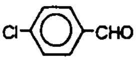
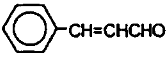
SELECTIVE REDUCTION OF FUNCTIONAL GROUPS

Chemoselective reduction of aldehydes in the presence of ketones is a very useful reaction in organic synthesis.

$Ba(BH_2S_3)_2$ has been used for selective reduction of aldehydes *vs* ketones with high chemoselectivity. In the presence of Li (OTf), the selectivity of the reaction increases and aldehydes are reduced much faster than ketones. However, high selectivity is observed for the reduction of ketones. Less sterically hindered ketones are easier reduced than the hindered ones with high selectivity (TableVII).

We have not been able to observe a pronounced differentiation between two different aldehydes with this reagent (Table VII). This reagent is able to show high selectivity for the reduction of azides in the presence of nitro groups with high selectivity at room temperature (Tables IV,7).

TABLE VII Selective reduction of structurally different carbonyl compounds with an equimolar amount of $Ba(BH_2S_3)_2$ in THF

Entry	*Subs. 1*	*Subs. 2*	*Time (h)*	*Conversion %*	
				Subs. 1	*Subs. 2*
1		PhCOMe	-^{ab}	100	0
2		PhCOMe	2	100	16
3		PhCOMe	2	100	20
4		PhCOMe	2	100	28
5			2.5^{b}	90	12
6		PhCOPh	2.5^{b}	100	0
7			2	100	0
8		PhCOMe	0.5^{b}	75	60
9			2	100	75
10		PhCOMe	0.5	100	50

a. The reaction was performed in the presence of 0.1 mole of LiOTf as a mild Lewis acid.
b. The reaction occurred under reflux condition.

CONCLUSION

In this study we have shown that unstable $NaBH_2S_3$could be relatively stabilized by cation exchange of group II elements. The most stable and more reactive hydride in this series is $Ba(BH_2S_3)_2$, which can be used effectively for the reduction of aldehydes, ketones, α,β-unsaturated carbonyl compounds, azides, epoxides, and nitro compounds. Functional groups, such as esters, carboxylic acids, oximes and amides remain unaffected by this reagent. Higher chemo- and regioselectivity is observed with this reagent in comparison with its parent compound; $NaBH_2S_3$.

Ease of preparation of the reagent from commercially available materials, easy work-up, high rate of the reaction, high yields of the products, and selectivity of the reactions are the strong practical points of this new modified borohydride reagent.

EXPERIMENTAL

All products were characterized by comparison of their IR and/ or ^{1}HNMR spectra and physical data with those of authentic samples. All yields refer to isolated products unless otherwise indicated. The purity determination of the substrates and the products and reaction monitoring were accomplished by TLC on silica gel polygram SIL/UV 254 plates or by GLC on Shimadzu model GC-8A and GC-14A instruments with hydrogen flame ionization detector. All solvents used in this study were thoroughly dried by the appropriate drying agents.

PREPARATION OF M $(BH_2S_3)_2$

A mixture of (7.56 g, 0.2 mol) $NaBH_4$ and sulfur (19.2 g, 0.6 mol) in anhydrous THF (50ml) was prepared in a flask (250ml) equipped with a condenser under argon atmosphere. The reaction was highly exothermic and a violent hydrogen gas evolution was observed therefore, cooling with an ice-water bath is obligatory to control the reflux. After the initial reaction had subsided, stirring at 25°C was continued for 30 min. Then, dry $SrCl_2$ or $BaCl_2$ (0.1 mol) was added to the reaction mixture and stirring at 25°C was continued for another 12 h. Solvent was then evaporated at room temperature under vacuum and the residual lump was washed three times with vigorous shaking with anhydrous petroleum ether. A yellow solid was then obtained in 80–85% yields, which should be protected from moisture and the air. The compounds are stable in an argon atmosphere at room temperature for several weeks and could be stored in a refrigerator for months.

REDUCTION OF 4-CHLOROBENZALDEHYDE TO 4-CHLOROBENZYL ALCOHOL WITH BA $(BH_2S_3)_2$, A TYPICAL PROCEDURE

In a round-bottomed flask (25ml) equipped with a magnetic stirrer, a solution of 4-chlorobenzaldehyde (0.14g, 1mmol) in dry THF (8–10ml) was prepared. $Ba(BH_2S_3)_2$ (0.47g, 1mmol) was added to the solution and the resulting mixture was stirred magnetically at room temperature for 2 h. The progress of the reaction was monitored by TLC (eluent; CCl_4/Et_2O, 5/1). After completion of the reaction, NaOH solution (5%, 10 ml) was added to the reaction mixture and stirred magnetically for 12 h. The reaction mixture was filtered and the filter cake was washed with THF (2 × 10ml). The filtrates were combined and dried over anhydrous Mg_2SO_4. Filteration and evaporation of the solvent afforded 4-chlorobenzyl alcohol in 92% yield (Table I).

REDUCTION OF 4-NITROACETOPHENONE TO 4-NITROPHENYLMETHYL CARBINOL, A TYPICAL PROCEDURE

In a round-bottomed flask (25ml) equipped with a magnetic stirrer and a condenser, a solution of 4-nitroacetophenone (0.165g, 1mmol) in dry THF (8–10ml) was prepared. The reducing agent (0.47g, 1mmol) was added to the resulting solution. The reaction mixture was stirred magnetically under reflux for 0.4 h. The progress of the reaction was monitored by TLC (eluent; $CC14/Et_2O$,5/1) After completion of the reaction NaOH solution (5%, 10ml) was added to the reaction mixture and was magnetically stirred about 10 h. The reaction mixture was filtered and the filter cake was washed with THF (2x 10ml). The filtrates were combined together and dried over unhydrous Mg_2SO_4 which after filteration and evaporation of the solvent afforded the desired alcohol in 90% yield (Table II).

REDUCTION OF CINNAMALDEHYDE TO 3-PHENYL-1-PROPANOL WITH $BA(BH_2S_3)_2$, A TYPICAL PROCEDURE

In a round-bottomed flask (25ml) equipped with a magnetic stirrer, a solution of cinnamaldehyde (0.13g, 1mmol) in dry THF (8–10ml) was prepared. The reducing agent (0.47g, 1mmol) was added to the resulting solution and was stirred magnetically at room temperature about 0.3 h. The progress of the reaction was monitored by TLC (eluent: CCl_4/Et_2O, 5/2). After completion of the reaction, NaOH solution (5%, 10ml) was added to the reaction mixture and was magnetically stirred about 10 h. The resulting mixture was filtered and the filter cake was washed with THF (2x10ml). The filtrates were combined and dried over anhydrous Mg_2SO_4. Filteration and evaporation of the solvent afforded 3-phenyl-1-propanol in 95% yield (Table III).

REDUCTION OF 4-NITROPHENYL AZIDE TO 4-NITROANILINE WITH $BA(BH_2S_3)_2$, A TYPICAL PROCEDURE

In a round-bottomed flask (25ml), equipped with a magnetic stirrer, a solution of azide (0.146g, 1mmol) in THF (8–10ml) was prepared. The reducing agent (0.47, 1mmol) was added to the resulting solution. The reaction was performed spontaneously. NaOH solution (5%, 10ml) was added to the reaction mixture and was magnetically stirred about 8 h. The mixture was filtered and the filter cake was washed with $CHCl_3$ (10ml). The combined filtrates were dried over anhydrous Mg_2SO_4 and filtered. Evaporation of the solvent afforded 4-nitro aniline in 90% yield (Table IV).

REDUCTION OF NITROBENZENE TO ANILINE WITH $BA(BH_2S3)_2$, A TYPICAL PROCEDURE

In a round-bottomed flask (25ml), equipped with a magnetic stirrer and a condenser, a solution of nitrobenzene (0.246g, 2mmol) in dry THF (8–

10ml) was prepared. The reducing agent (0.71g, 1.5mmol) was added to the solution in four portions in 20 min. intervals. The reaction mixture was stirred magnetically under reflux conditions about 1.3 h. The progress of the reaction was monitored by TLC (eluent; CCl_4/Et_2O; 3/1). After completion of the reaction, a solution of NaOH (5%, 15ml) was added to the reaction mixture and was magnetically stirred about 10 h. The mixture was filtered and the filter cake was washed with $CHCl_3$ (10ml). The combined filtrates were dried over anhydrous $MagSO_4$ which after filteration and evaporation of the solvent afforded almost pure aniline in 98% yield (Table V).

REDUCTION OF STYRENE OXIDE TO BIS-(2-HYDROXYETHYLPHENYL) DISULFIDE WITH $BA(BH_2S_3)_2$, A TYPICAL PROCEDURE

In a round-bottomed flask (25ml), equipped with a magnetic stirrer, a solution of epoxide (0.12g, 1mmol) in dry THF (8–10ml) was prepared. The reducing agent (0.47g, 1mmol) was added to the solution and was stirred magnetically at room temperature for 0.5 h. The progress of the reaction was monitored by TLC (eluent; CCl_4/Et_2O,5/1). After completion of the reaction, a solution of 5% NaOH (10ml) was added to the reaction mixture and was magnetically stirred about 10 h. The reaction mixture was filtered and the filter cake was washed with $CHCl_3$(15ml). The combined filtrates were dried over anhydrous Mg_2SO_4 and filtered. Evaporation of the solvent afforded symmetrical bis-(2-hydroxyethylphenyl) disulfide in 90% yield (Table VI).

Acknowledgements

The authors are grateful to National Research Council of I.R. Iran for the grant no. 462 and a grant from Shiraz University Research Council for the support of this work.

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