

Reaction of lithium tris(*tert*-butylthiolato)hydridoaluminate with selected organic compounds containing representative functional groups

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Abstract The approximate rates and stoichiometry of the reaction of lithium tri(2-methyl-2-propanethioxy)aluminum hydride (**LTBSA**) with selected organic compounds containing representative functional groups under the standardized conditions (tetrahydrofuran, 0 °C) were studied in order to define the reducing ability of **LTBSA** also compared with those of the parent lithium aluminum hydride (**LAH**) and lithium *t*-butoxyaluminum hydride (**LTBA**).

Keywords

Lithium tri(2-methyl-2-propanethioxy)aluminum hydride · Selective reduction · Organic functional groups · Li(*t*-BuS)₃AlH

Introduction

The introduction of alkoxy- [1–3] or dialkylamino- [4–7] substituents into lithium aluminum hydride (**LAH**) modifies its reducing capacity [8–14] to make possible a number of selective reductions of considerable utility in synthetic work [2, 15–25].

Similarly, the alkylthio-substituted derivatives of lithium aluminum hydride seem to exhibit reducing properties different from those of the parent reagent and/or the alkoxy derivatives. The present study was undertaken to examine

the effect of alkylthio substituents on the reducing action of lithium aluminum hydride. As a representative we chose *tert*-butylthio group and prepared lithium tris(*tert*-butylthiolato)hydridoaluminate (**LTBSA**). This paper describes the systematic exploration of the reaction of **LTBSA**, one of the class of alkylthio derivatives, with the standard list of organic compounds containing common functional groups under the standardized conditions (tetrahydrofuran, 0 °C) in order to define its reducing characteristics and compare with those of **LAH** [8] and lithium tri(*t*-butoxy)aluminum hydride (**LTBA**) [10].

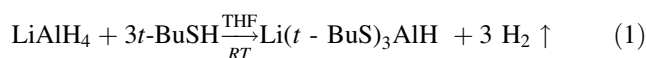
Results and discussion

Preparation of Lithium Tris(*tert*-butylthiolato)hydridoaluminate (**LTBSA**)

The reagent, **LTBSA**, was prepared readily from the reaction of 1 mole of lithium aluminum hydride with 3 moles of 2-methyl-2-propanethiol in THF at room temperature (Eq. 1). The reagent is very stable under the reaction conditions. The ²⁷Al NMR spectrum of **LTBSA** in THF showed a broad singlet at δ 129 ppm relative to Al(H₂O)₆³⁺.

Aldehydes and ketones (Table 1)

The simple aldehydes examined were readily reduced with 10% excess reagent at 0 °C to produce the corre-



sponding alcohols in a quantitative yield. However, the reaction of the ketones examined was relatively slow,

We dedicate this manuscript to Prof. Jack Harrowfield and Dr. Jacques Vicens in celebration of their 65th birthdays.

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Table 1 Reaction of representative aldehydes and ketones with lithium tris(*tert*-butylthiolato)hydridoaluminate in tetrahydrofuran at 0 °C

Compound	Time (h)	Yield of alcohol (%) ^a
Hexanal	1	90
	3	99
	6	99
	0.5 ^b	100
	1 ^b	100
Benzaldehyde	1	98
	3	100
	6	100
	0.5 ^b	99
	1 ^b	99
2-Heptanone	1	68
	3	72
	6	74
	24	82
	0.5 ^b	85
	1 ^b	99
	3 ^b	99
Acetophenone	1	78
	3	82
	6	87
	0.5 ^b	88
	1 ^b	98
	3 ^b	99

Ten % excess reagent utilized, except where otherwise indicated; *ca.* 0.5 M solution

^a GC yields with a suitable internal standard

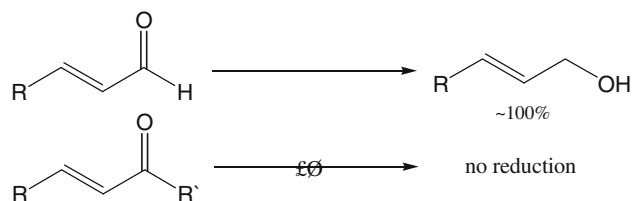
^b Two equiv of reagent utilized

requiring more excess reagent (2 equiv) for completion of the reduction.

The reactivity of **LTBSA** toward carbonyl compounds appears to be very much milder than that of **LAH** [8], even milder than that of **LTBA** [10]. **LTBA** reduces both aldehydes and ketones readily under similar reaction conditions.

Enals and enones (Table 2)

The most interesting reduction characteristics of **LTBSA** seem to be the selectivity in the reaction of α,β -unsaturated aldehyde (enals) and ketones (enones). Thus, the reagent reduced α,β -unsaturated aldehydes cleanly to the corresponding allylic alcohols: the selectivity appears perfect. However, α,β -unsaturated ketones examined are absolutely inert to this reagent (Eq. 2).



Generally, metal complex hydrides including **LAH** [8] cannot discriminate between α,β -unsaturated aldehydes and ketones: both the aldehydes and ketones are reducible. Furthermore, attack on the carbon–carbon double bond of the compound is frequently observed. However, a new type of Meerwein–Ponndorf–Verley (**MPV**) reagents, such as diisopinocampheylborane derivatives and diisobutylalane derivatives, reduce a variety of α,β -unsaturated carbonyl compounds to the corresponding allylic alcohols in an essentially 100% purity [26, 27]. Especially, *B*-alkoxy- and *B*-hydroxydiisopinocampheylboranes [28] can discriminate between α,β -unsaturated aldehyde and ketones. Thus, such reagents reduce α,β -unsaturated aldehydes readily to produce the corresponding allylic alcohols while α,β -unsaturated ketones being essentially stable, such as is encountered with **LTBSA**. **LTBA** also reacts immediately with cinnamaldehyde with using one equiv of hydride, however, no more data is available [10].

Stereochemistry in the reduction of cyclic ketones (Table 3)


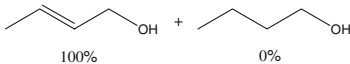
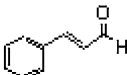
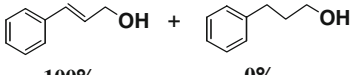

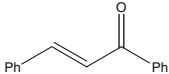
The stereoselectivity of the reagent toward cyclic ketones was also examined, and the results and those of **LAH** [29, 34] and **LTBA** [29–33] for comparison are summarized. The introduction of *tert*-butylthio group enhances the stereoselectivity to a large extent. These results are rather unexpected, because the introduction of *t*-butoxy group into **LAH** does not show any significant enhancement in the stereoselectivity.

The stereoselectivity achieved by **LTBSA** appeared to be higher than that performed by **LTBA**, presumably due to the relatively bigger steric size of sulfur atom than that of oxygen atom. Especially, the selectivity for 2-*t*-butylcyclohexanone is excellent to provide the *cis*-epimer exclusively.

Carboxylic acids and acyl derivatives (Table 4)

The reaction of carboxylic acids with excess reagent at 0 °C evolved an equivalent amount of hydrogen slowly, and the subsequent reduction also proceeded slowly to produce the corresponding alcohols. A different phenom-

Table 2 Reaction of representative α,β -unsaturated aldehydes and ketones with lithium tris(*tert*-butylthiolato)hydridoaluminate in tetrahydrofuran at 0 °C

Compound	Time (h)	Total yield (%) ^a	Products ^b
	24	99.9	
	24	99.9	
	24	0	
	24	0	

Ten % excess reagent utilized

^a Analyzed by GC using a suitable internal standard^b Normalized**Table 3** Stereochemistry in the reduction of representative cyclic ketones with lithium tris(*tert*-butylthiolato)hydridoaluminate in tetrahydrofuran at 0 °C

Compound	Time (h)	Total yield of alcohol (%)	Ratio of less stable isomer (%) ^a	Ratio of less stable isomer (%)	
				LiAlH ₄ ⁱ	Li(<i>t</i> -BuO) ₃ AlH ^j
2-Methylcyclohexanone	1 ^b	98	51 ^e	24	30–36
	1 ^c	100	54 ^e		
3-Methylcyclohexanone	1 ^b	97	29 ^f	16	17
	1 ^c	99.9	27 ^f		
4-Methylcyclohexanone	1 ^b	97	30 ^e	17	10
	1 ^c	100	31 ^e		
2- <i>t</i> -Butylcyclohexanone	24 ^b	72	88 ^e		
	24 ^c	86	>99.5 ^e		
	24 ^{c,d}	98	>99.5 ^e		
4- <i>t</i> -Butylcyclohexanone	1 ^b	99	23 ^e	8	9
	1 ^c	100	22 ^e		
3,3,5-Trimethylcyclohexanone	1 ^b	88	83 ^e	83	88–95
	1 ^c	99	83 ^e		
	1 ^{b,c}	100	82 ^e		
Camphor	24 ^b	100	91 ^g	92	94
Norcamphor	3 ^b	100	75 ^h	89	94

Determined by GC using a suitable internal standard^a Normalized^b Ten % excess reagent utilized^c Two equiv of reagent utilized^d At room temperature^e *Cis* isomer^f *Trans* isomer^g *Exo* isomer^h *Endo* isomerⁱ Data taken from Ref. [29] and [34]^j Data taken from Ref. [29]

enon was observed in the reaction of carboxylic acids with **LTBA** [10]: carboxylic acids evolve hydrogen slowly, but they do not undergo reduction.

The reaction of acid chlorides with 2 equiv of the reagent at 0 °C readily produces the corresponding alcohols. It is noteworthy that a limited amount of **LTBA** [10]

Table 4 Reaction of representative carboxylic acid and acyl derivatives with lithium tris(*tert*-butylthiolato)hydridoaluminate in tetrahydrofuran

Compound	Temp. (°C)	Time (h)	Total yield (%)	Products
Benzoic acid ^b	0	6	53	Benzyl alcohol
Caproic acid ^b	0	6	49	1-Hexanol
Benzoyl chloride	0 ^c	0.5	98	Benzyl alcohol
	0 ^d	0.5	52	17% Benzaldehyde + 35% benzyl alcohol
	-78 ^d	0.15	53	24% Benzaldehyde + 29% benzyl alcohol
Caproyl chloride	0 ^c	0.5	97	1-Hexanol
	0 ^d	0.5	52	19% Hexanal + 33% 1-hexanol
	-78 ^d	0.15	51	29% Hexanal + 22% 1-hexanol

^a Analyzed by GC using a suitable internal standard^b Four equivalents of reagent utilized. An equivalent of hydrogen evolved slowly^c A 2.1 equivalent of reagent utilized^d A 1.1 equivalent of reagent utilized

and sodium tri(*t*-butoxy)aluminum hydride (STBA) [35] at -78 °C provide a convenient tool for synthesis of aldehydes from acid chlorides. In the present study, we also examined LTBSA for such possibility. However, this reagent did not show any satisfactory results to give a mixture of the corresponding aldehyde and alcohol.

Esters (Table 5)

Both ethyl caproate and ethyl benzoate undergo the reduction only at a slow rate even with a large excess amount of LTBSA, showing 60–85% yield of the

Table 5 Reaction of representative esters and lactones with lithium tris(*tert*-butylthiolato)hydridoaluminate in tetrahydrofuran

Compound	Reagent/compd	Temp (°C)	Time (h)	Yield of alcohol (%) ^a
Ethyl caproate	1.1	0	24	18
			25	40
			72	81
	4.0	0	24	27
			25	45
			72	85
Ethyl benzoate	1.1	0	24	10
			25	13
			72	20
	4.0	0	24	27
			25	38
			72	61
Phenyl acetate	1.1 ^b	0	24	45
	2.0	25	1	99.9
Isopropenyl acetate	1.1	0	0.5	40
			24	43
	2.0	25	1	100

^a Analyzed by GC with a suitable internal standard^b Sixty % of acetaldehyde was formed within 1 h at 0 °C, but only a trace amount of acetaldehyde was detected in 3 h at 0 °C

corresponding alcohols. However, the reduction of phenyl acetate and isopropenyl acetate is far faster than that of other esters. Thus, the reagent reduces both acetates to ethanol within 1 h at 25 °C.

It is quite interesting to note that, when phenyl acetate was treated with a limited amount of the reagent at 0 °C, *ca.* 60% of acetaldehyde was formed in 1 h but the aldehyde was disappeared as the reaction proceeded. This suggests the possibility that the reaction might be proceeding in two successive stages.

A similar phenomenon is also observed in the reaction of esters with LTBA [10]. LTBA also showed a low reactivity to esters.

Epoxides (Table 6)

All of the epoxides examined showed absolutely no reactivity toward the reagent in 24 h at 0 °C. These results are rather surprising, because even LTBA reacts slowly [10].

Amide and Nitriles (Table 7)

Primary amides, such as caproamide and benzamide liberated partial hydrogen, but no reduction proceeded. Even the relatively reactive tertiary amides, such as *N,N*-dimethylcaproamide and *N,N*-dimethylbenzamide failed to indicate any reaction under the standard conditions. Moreover, the nitriles examined did not react with the reagent.

Table 6 Reaction of representative epoxides with lithium tris(*tert*-butylthiolato)hydridoaluminate in tetrahydrofuran at 0°C

Compound	Time (h)	Reduction product ^a
1,2-Butylene oxide	24	None
Styrene oxide	24	None
Cyclohexene oxide	24	None

Ten % excess reagent utilized^bAnalyzed by GC

Table 7 Reaction of representative amides and nitriles with lithium tris(*tert*-butylthiolato)hydridoaluminate in tetrahydrofuran at 0 °C

Compound	Reagent/ compd	Time (h)	Reduction product ^a
Caproamide	4	72	None ^b
Benzamide	4	72	None ^c
<i>N,N</i> -Dimethyl caproamide	4	72	None
<i>N,N</i> -Dimethylbenzamide	4	72	None
Capronitrile	4	72	None
Benzonitrile	4	72	None

^a Analyzed by GC ^bAccompanied with 1.53 equiv of hydrogen evolution in 6 h ^cAccompanied with 1.47 equiv of hydrogen evolution in 6 h

These results are quite similar to those obtained by **LTBA** with one exception [10]. Thus, primary amides neither liberate hydrogen, nor undergo reduction with **LTBA**. Both tertiary amides and nitriles are also inert toward **LTBA**.

Other nitrogen compounds (Table 8)

Among the nitrogen compounds examined, only nitro compound such as 1-nitropropane and nitrobenzene reacted relatively fast to produce the corresponding amine and hydrazo compound, respectively. However, other nitrogen compounds such as azobenzene, cyclohexanone oxime, phenyl isocyanate and pyridine were absolutely inert to the reagent.

The results obtained from the reaction of nitrogen compounds with the reagent appear to be quite different from those obtained with **LTBA** [10]. Thus, **LTBA** reduces 1-nitropropane, whereas nitrobenzene is inert toward the reagent. Phenyl isocyanate also shows a partial reduction with **LTBA**, but does not react with **LTBSA**.

Table 8 Reaction of representative other nitrogen compounds and their derivatives with lithium tris(*tert*-butylthiolato)hydridoaluminate in tetrahydrofuran

Compound	Reagent/ comp	Temp. (0 °C)	Time (h)	Product	Yield (%) ^a
1-Nitropropane	6	25	1		100 ^b
Nitrobenzene	6	25	24	PhNHNHPh	75 ^c
			72		100
Azobenzene	4	0	24		None
Cyclohexanone oxime	4	0	24		None ^d
Phenyl isocyanate	4	0	24		None
Pyridine	4	0	24		None

^a Analyzed by GC with a suitable internal standard^bA 0.71 equiv of hydrogen evolved^cA 0.45 equiv of hydrogen evolved^dA 0.92 equiv of hydrogen evolved

Sulfur compounds (Table 9)

Disulfides, such as diphenyl disulfide and di-*n*-butyl disulfide, were reduced readily to produce 2 equiv of the corresponding thiols with an accompanied slow evolution of hydrogen. On the other hand, other sulfur compounds examined, such as thioethers, sulfoxides and sulfones, showed no evidence of reaction.

LTBA also shows a similar trend in the reaction of sulfur compounds, except that di-*n*-butyl disulfide did not react but diphenyl disulfide is much more reactive utilizing one mole of hydride for reduction and one mole for hydrogen evolution in 6 h at 0 °C.

Conclusions

The reducing properties of lithium tris(*tert*-butylthiolato)hydridoaluminate (**LTBSA**) in tetrahydrofuran are now broadly characterized and compared with those of lithium tri(*t*-butoxy)aluminum hydride (**LTBA**). The introduction of *tert*-butylthio (*t*-BuS-) group into lithium aluminum hydride (**LAH**) diminishes the reaction power tremendously and modifies the reducing pattern of the parent **LAH**, which subsequently induces unique reducing characteristics of the reagent. Generally, **LTBSA** shows a relatively milder reducing power than that of **LTBA**. However, the reducing characteristics of **LTBSA** appear to be quite different from those of **LTBA**. Such a difference originates only from one atom exchange between oxygen and sulfur, which serves as a bridge for connecting *t*-butyl group to aluminum. Therefore, the present results are probably of more theoretical than practical significance.

However, the appearance of such a new type of reducing agent might be useful for devising a new procedure to synthesize a multifunctional complex molecule.

Table 9 Reaction of representative sulfur compounds with lithium tris(*tert*-butylthiolato)hydridoaluminate in tetrahydrofuran at 0 °C

Compound	Reagent/ compd	Time (h)	Product	Yield (%) ^a
Diphenyl disulfide	1.1	24	Benzenethiol	41
	2.2	1		199 ^b
Di- <i>n</i> -butyl disulfide	2.2	1	Butanethiol	201 ^c
Phenyl <i>n</i> -propyl sulfide	1.1	24		0
Dimethyl sulfoxide	1.1	24		0
Diphenyl sulfone	2	24		0

^a Analyzed by GC with a suitable internal standard^bA 0.47 equiv of hydrogen evolved in 1 h, but an equivalent of hydrogen evolution completed in 24 h^cA 0.44 equiv of hydrogen evolved in 1 h

Experimental section

All glassware was predried at 140 °C for at least 9 h, assembled hot, dried further with a flame, and cooled under the stream of nitrogen. All reactions were carried out under the static pressure of dry nitrogen in flask fitted with a septum-covered side arm with use a standard technique for handling air-sensitive materials [36]. Tetrahydrofuran (THF) was dried over sodium-benzophenone ketyl and distilled prior to use. ^{27}Al NMR spectra recorded on a Bruker WP 80 SY spectrometer, and chemical shift is reported relative to $\text{Al}(\text{H}_2\text{O})_6^{3+}$. GC analyses were performed using a Varian CP-3800 gas chromatograph (FID detector) with use of 30 m \times 0.25 mm capillary column of DB-Wax and 25 m \times 0.25 mm capillary column of HP-FFAP.

Preparation of a solution of tri(2-methyl-2-propanethioxy)aluminum hydride (LTBSA) in THF

An oven-dried, 250-mL, round-bottomed flask with a side arm, equipped with a condenser leading to a mercury bubbler was flushed dry nitrogen and maintained under a static pressure of nitrogen. To this flask was charged 100 mL of a solution of LiAlH_4 in THF (2.0 M, 200 mmol), and followed by dropwise addition of 55.8 g of 2-methyl-2-propanethiol (620 mmol) via a double-ended needle with vigorous stirring at 25 °C until the hydrogen evolution was completed. The resulting clear solution was standardized by hydrolyzing an aliquot with 3 *N* HCl–THF mixture to be 1.2 M, and kept under nitrogen at 0 °C. The THF solution of LTBSA was characterized by a characteristic absorption in the IR at around 1,640 cm^{-1} ($\nu_{\text{Al-H}}$) and by a broad single at δ 129 ppm in the ^{27}Al NMR relative to $\text{Al}(\text{H}_2\text{O})_6^{3+}$.

General procedure for determination of rates and stoichiometry

The reaction of 2-heptanone is described as a representative example. In the usual set-up was placed 10 mL of 1.2 M LTBSA (12 mmol) in THF and the flask was maintained at 0 °C with the aid of an ice-water bath. To the flask 14 mL of a precooled THF solution to 0 °C containing 0.72 g (6 mmol) of 2-heptanone and tridecane (2 mmol) as an internal standard was added with stirring. At the indicated time intervals, an aliquot of the reaction mixture was withdrawn with the aid of hypodermic syringe and quenched with 2 *N* HCl. The aqueous layer was saturated with K_2CO_3 and the organic layer was dried with anhydrous MgSO_4 . GC analysis of the organic layer showed the presence of 85, 99 and 99% of 2-heptanol at the 0.5, 1 and 3 h time intervals, respectively (Table 1).

In cases where a maximum yield of the reduction product was apparent, no further analysis of the product was performed.

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