Selective Reduction by Lithium Bis- or Tris(dialkylamino)aluminum Hydrides. VIII. Reaction of Lithium Tripiperidinoaluminum Hydride in Tetrahydrofuran with Selected Organic Compounds Containing Representative Functional Groups

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The approximate rates and stoichiometry of the reaction of excess lithium tripiperidinoaluminum hydride (LTPDA), an alicyclic aminoaluminum hydride, with selected organic compounds containing representative functional groups under the standardized conditions (tetrahydrofuran, 25°) were examined in order to define the reducing characteristics of the reagent for selective reductions. The reducing ability of LTPDA was also compared with those of the parent lithium aluminum hydride (LAH) and lithium tris(diethylamino)aluminum hydride (LTDEA), a representative aliphatic aminoaluminum hydride. In general, the reactivity of LTPDA toward organic functionalities is weaker than LTDEA and much weaker than LAH. LTPDA shows a unique reducing characteristics. Thus, benzyl alcohol, phenol and thiols evolve a quantitative amount of hydrogen rapidly. The rate of hydrogen evolution of primary, secondary and tertiary alcohols is distinctive. LTPDA reduces aldehydes, ketones, esters, acid chlorides and epoxides readily to the corresponding alcohols. Quinones, such as *p*-benzoquinone and anthraquinone, are reduced to the corresponding diols without hydrogen evolution. Tertiary amides and nitriles are also reduced readily to the corresponding amines. The reagent reduces nitro compounds and azobenzene to the amine stages. Disulfides are reduced to thiols, and sulfoxides and sulfones are converted to sulfides. Additionally, the reagent appears to be a good partial reducing agent to convert primary carboxamides into the corresponding aldehydes.

Introduction

Recently, we have synthesized and characterized the reducing properties of the acyclic dialkylamino-substituted derivatives of lithium aluminum hydride (LAH),[1] lithium tris(dialkylamino)aluminum hydrides ($Li(R_2N)_3AlH$; R=Et, Bu, Hex). The addition of 3 moles of a secondary aliphatic amine to 1 mole of LAH in tetrahydrofuran (THF) provides a simple, convenient means of preparing such derivatives[2] which exhibit reducing properties significantly different from those of the parent LAH[3] to show unique reducing potentials for selective reduction of organic functionalities. Additionally, we synthesized an alicyclic derivative, lithium tripiperidinoaluminum hydride (LTPDA), and applied for the reduction of common organic functional groups. In this course we found that the reagent reduces primary carboxamides to the corresponding aldehydes in good yields.[1-d] Although LTPDA is highly promising for such applications, a full characterization of the reducing properties of the reagent has not been investigated, that probably limits the utilization of this reagent in organic synthesis. Accordingly, we decided to undertake a detailed study of the full scope of the reducing characteristics of this reagent under standardized conditions (THF, 25°). Herein, we report the characterization of reducing properties of lithium tripiperidinoaluminum hydride (LTPDA), an alicyclic aminoaluminum hydride, and the comparision of its reducing properties with those of the parent lithium aluminum hydride (LAH) and lithium tris(diethylamino)aluminum hydride (LTDEA)[1-g] as a representative of acyclic aminoaluminum hydrides.

Experimental Section

The reaction flasks and other glassware used for the experiments were predried at 140° for several hours, assembled while hot, and cooled under a stream of dry nitrogen. All reactions were carried out under a static pressure of nitrogen in flasks fitted with a septum-covered sidearm with use of standard techniques for handling air-sensitive materials.[4] Hypodermic syringes were used at all times to transfer solutions. THF was dried over sodium-benzophenone ketyl prior to use. Most of the organic compounds utilized in this study were commercial products of the highest purity. They were further purified by distillation or recrystallization when necessary. Some compounds, such as 1-methylcyclohexene oxide, were synthesized by using standard procedures. lithium aluminum hydride (LAH) was purchased from Aldrich Chemical Co. and used as received. ^{27}Al NMR spectra were recorded on a Bruke AMX 300 spectrometer, and chemical shifts are reported relative to Al $(H_2O)_6^{3+}$. IR spectra were taken with a Perkin-Elmer 1330 spectrophotometer equipped with a sealed liquid cell. GC analyses were performed using a Hewlett-Packard 5790 FID chromatography with use of 12 ft.×0.125 in. column of 15% THEED on a 100-200 mesh Supelcoport or 10% Carbowax 20 M on 100-200 mesh Supelcoport.

Preparation of Lithium Tripiperidinoaluminum hydride (LTPDA). An oven-dried, 500 mL, round-bottom flask with a sidearm, equipped with a condenser leading to a mercury bubbler, was flushed with dry nitrogen and maintained under a static pressure of nitrogen. To this

flask was charged 100 mL of $LiAlH_4$-THF (2.0 M, 200 mmol), and followed by dropwise addition of 52.4 g of piperidine (615 mmol) as a neat *via* a double-ended needle with vigorous stirring. The mixture was stirred for 3 h at room temperature until the hydrogen evolution was completed. The resulting clear solution was standardized by hydrolyzing an aliquot with 2 N H_2SO_4-THF mixture to be 1.6 M, and kept under nitrogen at 0°. The THF solution of LTPDA was characterized by a characteristic absorption in the IR at around 1665 cm^{-1} (ν_{Al-H}) and by a broad singlet at δ 124 ppm in ^{27}Al NMR.

General Procedure for Determination of Rates and Stoichiometry. The following procedure was used for quantitative studies. The reduction of caproaldehyde is described as an example of the experimental procedure. A dried, 100 mL, round-bottom flask fitted with a sidearm and a condenser leading to a gas buret was immersed in a water bath at 25°. The flask was charged with 10.0 mL (16 mmol) of a 1.6 M THF solution of LTPDA and 2.0 mL of THF. Finally, 4.0 mL of a 1.0 M solution of caproaldehyde in THF was injected into the reaction flask. Now the reaction mixture was 1.0 M in the reagent and 0. 25 M in caproaldehyde. The hydrogen evolved was collected in the buret and measured (0.01 mmol). After 0.5 h, a 4.0 mL aliquot of the reaction mixture (1.0 mmol of the compound) was removed with a hypodermic syringe and injected into a 2 N H_2SO_4-THF mixture to hydrolyze residual hydride. The hydrogen evolved amounted to 3.39 mmol, which indicates that 0.60 mmol of hydride was used for reduction per mmol of compound. After 3 h, the analysis showed that 1.00 mmol of hydride was used for reduction, which indicated that the compound had been reduced to the corresponding alcohol. The results are summarized in Table 2.

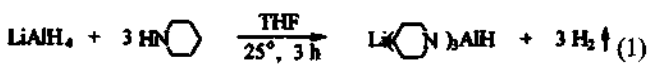
Reduction of Epoxides. The following procedure for the reduction of 1,2-butylene oxide illustrates the technique utilized in cases where the reaction mixture was subjected to identification of products.

Being utilized the above general procedure, the reduction of 1,2-butylene oxide with LTPDA was performed for 1 h at 25°. The reaction mixture was then hydrolyzed with 2 N HCl and the organic layer was taken up in ether. The GC analysis showed only the presence of 2-butanol.

In cases where a single product in the reaction mixture was apparent, we did not perform the product identification further.

Results and Discussion

Lithium tripiperidinoaluminum hydride (LTPDA) was easily prepared in a pure form from the addition of 3 moles of piperidine to 1 mole of lithium aluminum hydride in tetrahydrofuran at room temperature (Eq. 1). The reagent is very stable under the reaction condition. No sign of disproportionation and hydride loss is observed while the reagent is kept under a static pressure of dry nitrogen, The ^{27}Al NMR spectrum of LTPDA in THF showed a broad singlet at δ 124 ppm relative to $Al(H_2O)_6^{3+}$.



The general procedure for the systematic study involved preparation of a reaction mixture of LTPDA (1.0 M in hydride) and the compound (0.25 M) under study in THF at 25°. Hydrogen evolution following addition of the compound to the reagent was measured by using a gasburet. A blank reaction was run under identical condition without addition of the compound. From time to time, aliquots were taken from the reaction mixture and analyzed for residual hydride by hydrolysis.[4] From the difference in the volume of hydrogen evolved in the two intervals, the hydride used by the compound for reaction was calculated. In this way, it was possible to calculate a value for the number of moles of the hydride consumed by the compound for hydrogen evolution and the number of moles of hydride utilized for the reduction.

Alcohols, Phenols, Amines, and Thiols (Active Hydrogen Compounds). All of the alcohols examined liberated hydrogen rapidly and quantitatively, with the exception of 3-ethyl-3-pentanol which evolved only 0.75 equiv of hydrogen in 72 h. The rate of hydrogen evolution for alcohols decreases in the order of primary > secondary > tertiary. This is in agreement with the usual interpretation that the acidity of the hydroxylic hydrogen in these alcohols decreases in this order.[5]

Phenol, 1-hexanethiol, and benzenethiol also evolved hydrogen rapidly and quantitatively. However, *n*-hexylamine liberated only 1 equiv of hydrogen rapidly within 1 h and no further hydrogen evolution was apparent thereafter. These results are summarized in Table 1.

LTDEA shows a similar trend in the reaction of alcohols and amines, but the thiols examined are absolutely inert to

Table 1. Reaction of Lithium Tripiperidinoaluminum Hydride with Representative Active Hydrogen Compounds in Tetrahydrofuran at 25 °C[a]

Compound	Time, h	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
1-Hexanol	0.5	0.99	0.99	0.00
	1.0	1.00	1.00	0.00
Benzyl alcohol	0.5	1.00	1.00	0.00
	1.0	1.00	1.00	0.00
3-Hexanol	0.5	0.43	0.43	0.00
	3.0	0.86	0.86	0.00
	6.0	1.00	1.00	0.00
3-Ethyl-3-pentanol	3.0	0.24	0.24	0.00
	24.0	0.52	0.52	0.00
	72.0	0.75	0.75	0.00
Phenol	0.5	0.91	0.91	0.00
	1.0	1.00	1.00	0.00
n-Hexylamine	0.5	0.90	0.90	0.00
	1.0	1.00	1.00	0.00
	3.0	1.00	1.00	0.00
1-Hexanethiol	0.5	1.00	1.00	0.00
Benzenethiol	0.5	0.97	0.97	0.00
	1.0	1.00	1.00	0.00

[a] 5.0 Mmol of compound was added to 20 mmol of the reagent (0.25 M in compound and 1.0 M in hydride). [b] Mmol per mmol of compound.

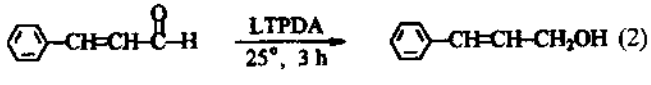
Table 2. Reaction of Lithium Tripiperidinoaluminum Hydride with Representative Aldehydes and Ketones in Tetrahydrofuran at 25 °C[a]

Compound	Time, h	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Caproaldehyde	0.5	0.01	0.61	0.60
	1.0	0.01	0.84	0.83
	3.0	0.01	1.01	1.00
Benzaldehyde	0.5	0.00	0.62	0.62
	1.0	0.00	0.88	0.88
	3.0	0.00	1.00	1.00
2-Heptanone	0.5	0.00	0.96	0.96
	1.0	0.00	1.00	1.00
Norcamphor	0.5	0.01	0.92	0.91
	1.0	0.01	1.01	1.00
Acetophenone	0.5	0.00	0.90	0.90
	1.0	0.00	1.00	1.00
Benzophenone	0.5	0.00	0.92	0.92
	1.0	0.00	1.00	1.00
Cinnamaldehyde	0.5	0.00	0.99	0.99
	1.0	0.00	1.00	1.00
	12.0	0.00	1.01	1.01

[a,b] See corresponding footnotes in Table 1.

LTDEA at 0°.[1-8] However, LAH evolves hydrogen immediately from reaction with all these avtive hydrogen compounds.[3]

Aldehydes and Ketones. The aldehydes and ketones examined utilized 1 equiv of hydride rapidly at 25° to proceed to the alcohol stage. Cinnamaldehyde, an α,β-unsaturated carbonyl compound, consumed 1 equiv of hydride immediately and no further hydride uptake was apparent even after 12 h. This means that LTPDA reduces the aldehyde group cleanly without affecting the double bond to produce cinnamyl alcohol (Eq. 2). These results are summarized in Table 2.



(2)

Both LTDEA and LAH reduce cinnamaldehyde to hydrocinnamyl alcohol stage rapidly even at 0°.[1-8,3]

Quinones. Two examples for quinones were examined and the results are summarized in Table 3. Thus, both *p*-benzoquinone and anthraquinone evolved no hydrogen and utilized rapidly 2 equiv of hydride for reduction at 25°. These results correspond to the reduction to the 1,4-dihydroxycyclohexadiene and 9,10-dihydro-9,10-anthracenediol stages, respectively. In general, the reduction of quinones with common boron and aluminum hydrides yields a mixture containing hydroquinones. Similarly, in the case of LTDEA,[1-8] no hydrogen evolution is observed during the reduction. Unlike these amino-derivatives, the parent LAH reduces the quinones with partial evolution of hydrogen to give a mixture of the corresponding hydroquinone and 1,4-dihyroxy-cyclohexadiene.[3]

Carboxylic Acids and Acyl Derivatives. Both caproic and benzoic acids liberated 1 equiv of hydrogen

Table 3. Reaction of Lithium Tripiperidinoaluminum Hydride with Representative Quinones in Tetrahydrofuran at 25 °C[a]

Compound	Time, h	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
p-Benzoquinone[c]	0.5[d]	0.00	0.82	0.82
	1.0	0.00	1.28	1.28
	3.0	0.00	1.63	1.63
	6.0	0.00	2.02	2.02
Anthraquinone[c]	0.5[e]	0.00	1.86	1.86
	1.0	0.00	2.00	2.00

[a,b] See corresponding footnotes in Table 1. [c] Batch reaction. [d] Color changed to dark green immediately followed by a formation of precipitate, and then color changed to violet. [e] Color changed to dark brown immediately.

slowly, requiring 6 h for completion. Moreover, only partial reduction of the acids was observed even in 5 or 7 days at 25° (the hydrazine analysis of the reaction mixture did not

Table 4. Reaction of Lithium Tripiperidinoaluminum Hydride with Representative Carboxylic Acids and Acyl Derivatives in Tetrahydrofuran at 25 °C[a]

Compound	Time, h	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Caproic acid	0.5	0.70	1.31	0.61
	3.0	0.87	1.71	0.84
	6.0	1.00	1.93	0.93
	24.0	1.00	2.04	1.04
	72.0	1.00	2.12	1.12
	168.0	1.00	2.27	1.27
Benzoic acid	0.5	0.77	1.36	0.59
	6.0	1.00	1.96	0.96
	24.0	1.00	2.09	1.09
	72.0	1.00	2.18	1.18
	120.0	1.00	2.24	1.24
Acetic anhydride[c]	0.5	0.00	1.62	1.62
	1.0	0.00	2.05	2.05
	6.0	0.00	2.64	2.64
	24.0	0.00	3.27	3.27
	72.0	0.00	4.00	4.00
Succinic anhydride[c]	0.5	0.00	1.52	1.52
	6.0	0.00	2.33	2.33
	24.0	0.00	3.01	3.01
	72.0	0.00	3.58	3.58
	120.0	0.00	4.00	4.00
Phthalic anhydride[c]	0.5	0.00	1.43	1.43
	3.0	0.00	2.24	2.24
	24.0	0.00	3.01	3.01
	72.0	0.00	3.80	3.80
	168.0	0.00	4.00	4.00
Caproyl chloride	0.5	0.02	1.98	1.96
	1.0	0.02	2.03	2.01
Benzoyl chloride	0.5	0.00	2.00	2.00
	1.0	0.00	2.00	2.00

[a,b] See corresponding footnotes in Table 1. [c] Hydride to compound ratio is 6 : 1.

Table 5. Reaction of Lithium Tripiperidinoaluminum Hydride with Representative Esters and Lactones in Tetrahydrofuran at 25 °C[a]

Compound	Time, h	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Ethyl caproate	0.5	0.00	1.52	1.52
	1.0	0.00	1.82	1.82
	3.0	0.00	2.00	2.00
Ethyl benzoate	0.5	0.00	1.52	1.52
	1.0	0.00	1.78	1.78
	3.0	0.00	2.00	2.00
Phenyl acetate	0.5	0.00	1.48	1.48
	3.0	0.00	2.00	2.00
γ-Butyrolacone	0.5	0.00	1.41	1.41
	3.0	0.00	1.67	1.67
	6.0	0.00	1.83	1.83
	24.0	0.00	2.02	2.02
Phthalide	0.5	0.00	0.90	0.90
	3.0	0.00	1.14	1.14
	12.0	0.00	1.17	1.17
	48.0	0.00	1.26	1.26
Isopropenyl acetate	0.5	0.00	1.99	1.99
	6.0	0.00	2.46	2.46
	24.0	0.00	2.63	2.63
	72.0	0.00	3.01	3.01

[a,b] See corresponding footnotes in Table 1.

show any aldehyde formation). Acid anhydrides consumed 2 equiv of hydride rapidly, with a slow reduction thereafter. Reduction of acid chlorides was completed rapidly to the corresponding alcohols. These results are summarized in Table 4.

Quite similar results are obtained with LTDEA. However, generally LTPDA is less reactive than LTDEA. LAH reduces these functionalities rapidly.[3]

Esters and Lactones. All of the esters examined reacted with LTPDA readily with the uptake of 2 equiv of hydride per mole of compound to be reduced to the alcohol stage. The reduction of γ-butyrolactone proceeded relatively fast to the corresponding diol, whereas phthalide utilized one hydride rapidly, with a second equiv of hydride being taken only quite slow. Isopropenyl acetate utilized 2 equiv of hydride very fast, and a third hydride consumed slowly. The results are summarized in Table 5.

The reaction of esters with LTDEA seems to be more selective: the reagent with a limiting amount transforms esters to aldehydes at −78° in good yields.[1,i] However, the parent LAH reduces these compounds exceedingly rapidly to alcohol stages.[3]

Epoxides. All of the epoxides examined utilized 1 equiv of hydride, undergoing rapid and quantitative reduction to the corresponding alcohols. The opening of the epoxide ring with this reagent proceeds with exceptional selectivity, yielding the Markovnikov alcohol exclusively. Such rate and selectivity are also observed with LTDEA.[1g] These results are summarized in Table 6.

Amides and Nitriles. Primary carboxamides, such as caproamide and benzamide, underwent reduction slowly

Table 6. Reaction of Lithium Tripiperidinoaluminum Hydride with Representative Epoxides in Tetrahydrofuran at 25 °C[a]

Compound	Time, h	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
1,2-Butylene oxide	0.5	0.00	0.98	0.98
	1.0[c]	0.00	1.00	1.00
Styrene oxide	0.5	0.00	0.99	0.99
	1.0[d]	0.00	1.00	1.00
Cyclohexene oxide	0.5	0.00	0.97	0.97
	1.0	0.00	1.00	1.00
1-Methylcyclohexene	0.5	0.00	0.99	0.99
	1.0[e]	0.00	1.00	1.00

[a,b] See corresponding footnotes in Table 1. [c] Only 2-butanol was detected. [d] 1-Phenylethanol (99%) and trace of 2-phenylethanol. [e] Only 1-methylcyclohexanol was detected.

with concurrent slow evolution of hydrogen. Caproamide evolved only 1 equiv of hydrogen in 12 h, whereas benzamide liberated 1 equiv of hydrogen rapidly, with the second being evolved only slowly. The reduction of primary carboxamide by LTPDA is quite interesting. The first hydride consumption for reduction was relatively fast with the second being quite slow, showing the possibility of the

Table 7. Reaction of Lithium Tripiperidinoaluminum Hydride with Representative Amides and Nitriles in Tetrahydrofuran at 25 °C[a]

Compound	Time, h	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Caproamide	0.5	0.72	1.29	0.57
	3.0	0.81	1.67	0.86
	12.0[c]	1.02	2.10	1.08
	24.0	1.02	2.27	1.25
	96.0	1.02	3.04	2.02
Benzamide	0.5	1.07	1.37	0.30
	6.0	1.64	2.33	0.69
	24.0[d]	1.93	2.93	1.00
	72.0	2.00	3.16	1.16
	120.0	2.00	3.25	1.25
N,N-Dimethylcaproamide	0.5	0.00	1.84	1.84
	1.0	0.00	2.00	2.00
N,N-Dimethylbenzamide	0.5	0.00	1.86	1.86
	1.0	0.00	2.00	2.00
Capronitrile	0.5	0.00	0.80	0.80
	3.0	0.00	1.10	1.10
	12.0	0.00	1.30	1.30
	48.0	0.00	1.52	1.52
	120.0	0.00	2.00	2.00
Benzonitrile	0.5	0.00	1.11	1.11
	3.0	0.00	1.59	1.59
	24.0	0.00	1.88	1.88
	48.0	0.00	2.01	2.01

[a,b] See corresponding footnotes in Table 1. [c] 66% of caproaldehyde was formed with 2 equiv of reagent at 25°. [d] 92% of benzaldehyde was formed with 3 equiv of reagent at 25°.

formation of aldehyde intermediate. Indeed, we applied this reagent successfully for the synthesis of aldehydes from the corresponding primary carboxamides.[1d] On the other hand, the reduction of tertiary carboxamides was quite fast, the uptake of 2 equiv of hydride being complete in 1 h. Both capronitrile and benzonitrile utilized 2 equiv of hydride slowly without hydrogen evolution. The experimental data are summarized in Table 7.

LTDEA shows also a similar trend toward amides and nitriles. The reaction of primary carboxamides with LTDEA provides the corresponding aldehydes in good yields at room temperature.[1c,f] LAH reacts with primary carboxamides with evolution of 2 equiv of hydrogen, followed by slow reduction. Furthermore, LAH reacts with capronitrile to evolve a partial hydrogen.[3] Again, the reactivity of LTPDA appears to be weaker than LTDEA.

Nitro Compounds and Their Derivatives. Both aliphatic and aromatic nitro compounds, such as 1-nitropropane and nitrobenzene, consumed 3 equiv of hydride readily for reduction with relatively slow evolution of hydrogen. The reaction utilizing 3 equiv of hydride for reduction and 3 equiv of hydride for hydrogen evolution corresponds to a reduction to amine and aniline stages, respectively. The slow hydrogen evolution woud be attributed to the low reactivity of the reagent toward the unknown intermediate which possesses active hydrogen. Azobenzene was also reduced slowly to aniline stage without hydrogen evolution. The results are summarized in Table 8.

Both LTDEA and LAH reduce nitrobenzene and azobenzene to the hydrazobenzene stage.[1g,3]

Other Nitrogen Compounds. Cyclohexanone oxime evolved no hydrogen, but consumed 1 equiv of hydride for reduction readily, apparently being reduced to the corresponding *N*-hydroxylamine stage. Phenyl isocyanate was rapidly reduced to formanilide stage in 1 h. LTPDA showed very little reactivity toward pyridine. On the other hand, 4-picoline *N*-oxide utilized 2 equiv of hydride for reduction without hydrogen evolution. These results are summarized in Table 9.

The reaction of these compounds with LTDEA shows similar results.[1g] However, LAH reduces cyclohexanone oxime to cyclohexylamine and phenyl isocyanate to N-methylaniline.[3]

Sulfur Derivatives. Both aliphatic and aromatic disulfides were rapidly reduced to the corresponding thiols with utilization of 2 equiv of hydride, one for reduction and the other for hydrogen evolution. Sulfoxides, such as dimethyl

Table 8. Reaction of Lithium Tripiperidinoaluminum Hydride with Representative Nitro Compounds in Tetrahydrofuran at 25 °C[a]

Compound	Time, h	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
1-Nitropropane[c,d]	0.5	0.64	1.89	1.25
	1.0	0.85	2.39	1.54
	6.0	1.37	3.60	2.23
	24.0	1.62	4.36	2.74
	72.0	1.82	4.83	3.01
Nitrobenzene[c,e]	0.5	1.12	3.15	2.03
	3.0	1.39	3.67	2.28
	12.0	1.67	4.34	2.67
	48.0	1.91	4.91	3.00
Azobenzene[f]	0.5	0.00	0.60	0.60
	3.0	0.00	0.86	0.86
	24.0	0.00	1.44	1.44
	72.0	0.00	1.64	1.64
	144.0	0.02	1.93	1.91

[a,b] See corresponding footnotes in Table 1. [c] Hydride to compound ratio is 6:1. [d] A brown color formed immediately. [e] A brown color formed and turned to light brown slowly. [f] Solution changed from reddish brown to dark brown.

Table 9. Reaction of Lithium Tripiperidinoaluminum Hydride with Representative Other Nitrogen Compounds in Tetrahydrofuran at 25 °C[a]

Compound	Time, h	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Cyclohexanone oxime	0.5	0.00	0.79	0.79
	3.0	0.00	1.09	1.09
	24.0	0.00	1.09	1.09
Phenyl isocyanate	0.5	0.00	0.87	0.87
	1.0	0.00	1.02	1.02
	6.0	0.00	1.02	1.02
Pyridine	0.5	0.00	0.08	0.08
	6.0	0.00	0.15	0.15
	24.0	0.00	0.18	0.18
	48.0	0.00	0.19	0.19
4-Picoline *N*-oxide	0.5	0.00	1.66	1.66
	1.0	0.00	1.91	1.91
	3.0	0.00	2.00	2.00

[a,b] See corresponding footnotes in Table 1.

Table 10. Reaction of Lithium Tripiperidinoaluminum Hydride with Representative Sulfur Derivatives in Tetrahydrofuran at 25 °C[a]

Compound	Time, h	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Di-*n*-butyl disulfide	0.5	0.98	1.99	1.01
	1.0	1.00	2.01	1.01
Diphenyl disulfide	0.5	0.99	1.99	1.00
	1.0	1.00	2.00	1.00
Dimethyl sulfoxide	0.5	0.00	0.84	0.84
	1.0	0.00	0.93	0.93
	3.0	0.00	1.01	1.01
Diphenyl sulfone	0.5	0.00	1.02	1.02
	1.0	0.00	1.43	1.43
	6.0	0.00	2.03	2.03
Methanesulfonic acid	0.5	1.00	1.00	0.00
	6.0	1.00	1.00	0.00
p-Toluenesulfonic acid monohydrate	0.5	2.30	2.30	0.00
	3.0	2.73	2.73	0.00
	12.0	3.00	3.00	0.00

[a,b] See corresponding footnotes in Table 1.

sulfoxide, were also readily reduced to the corresponding sulfides. Diphenyl sulfone consumed 2 equiv of hydride for reduction. Methanesulfonic acid and *p*-toluenesulfonic acid monohydrate liberated hydrogen relatively fast: the former evolved 1 equiv of hydrogen within 0.5 h and the latter evolved 3 equiv of hydrogen within 12 h. These results are summarized in Table 10.

LTDEA shows a very interesting characteristics in the reduction of disulfides: the reagent reduces disulfides to thiols at an exceedingly fast rate at 0° without evolution of any hydrogen. However, LAH reduces these compounds readily with evolution of hydrogen.

Conclusion

The reducing properties of lithium tripiperidinoaluminum hydride (LTPDA), an alicyclic aminoaluminum hydride, are now fully characterized and also compared with those of lithium tris(diethylamino)aluminum hydride (LTDEA), a representative aliphatic aminoaluminum hydride, and the parent lithium aluminum hydride (LAH). The reducing power of LTPDA is weaker than LTDEA and much weaker than LAH. LTPDA is a mild selective reducing agent. The reagent reduces a variety of organic functional groups under the mild reaction conditions. Consequently, this reagent should be a choice of reagent in the selective reduction of a particular function in organic synthesis.

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