Reaction of Aluminum Hydride–Triethylamine Complex with Selected Organic Compounds Containing Representative Functional Groups

Jin Soon Cha* and Herbert C. Brown†

Department of Chemistry, Yeungnam University, Kyongsan 712-749, Republic of Korea

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The addition of triethylamine to a solution of aluminum hydride in tetrahydrofuran (THF), which was prepared by the addition of a calculated amount of hydrogen chloride in diethyl ether to solutions of sodium aluminum hydride in THF, provides very stable solutions of aluminum hydride–triethylamine complex (AHTEA). The reducing power of AHTEA complex in tetrahydrofuran toward 59 selected organic compounds containing representative functional groups under practical conditions (tetrahydrofuran, room temperature, the quantitative amount of reagent to compound) has been investigated. In this way, we have established that quantitative reduction of various organic functionalities can be readily achieved using the calculated quantity of AHTEA to avoid the use of excess reagent. This permits ready use of the aluminum hydride reagent in organic synthesis with high convenience and efficiency, with the possibility of an improved selectivity than that of aluminum hydride itself in tetrahydrofuran.

Aluminum hydride, a very interesting and valuable reducing agent, has been widely used in numerous applications in organic synthesis.[1] Jorgenson first reported the comparison in the reducing properties between lithium aluminum hydride and aluminum hydride on the reduction of cinnamaldehyde,[2] and Brown and Yoon reported a systematic study on the reducing properties of aluminum hydride in THF, comparing its reducing characteristics to that of lithium aluminum hydride in the 1960's.[3]

Even though aluminum hydride has found numerous applications in organic synthesis, the lack of availability commercially or a simple procedure for making it has caused it to be used less than its valuable reducing properties suggest.

The usual laboratory procedure for the synthesis of aluminum hydride solution in THF involves treatment of a standardized solution of lithium aluminum hydride in THF with a theoretical quantity of 100% sulfuric acid (eq 1).[3] Even though this procedure provides a pure aluminum

$$2LiAlH_4 + H_2SO_4 \xrightarrow{THF} 2AlH_3 + Li_2SO_4\downarrow + 2H_2\uparrow \quad (1)$$

hydride solution in THF, there has been some resistance to the use of 100% sulfuric acid with lithium aluminum hydride. Furthermore, the aluminum hydride solution in THF possesses a significant problem: such solutions undergo slow THF cleavage at room temperature.[3] Therefore, the aluminum hydride solution should be maintained at 0 °C, both for storage and reaction.

Consequently, there has been a need for development of a simple, convenient procedure for the preparation of solutions of aluminum hydride in THF and preparation of a stable aluminum hydride reagent, easy to ship and use. Aluminum hydride–amine complexes would appear to meet this requirement.

The first observation that aluminum hydride forms a 1:1 and a 1:2 complex with trimethylamine was reported by Wiberg and co-workers in 1952.[4] Several other 1:1 complexes with tertiary alkylamines were reported later.[5] Generally, pure aluminum hydride–amine complexes are thermally stable[4,5b,e,g] and very stable in solutions such as in toluene,[5h] benzene,[5h] and even THF.

The reducing power of aluminum hydride–amine complex was first reported by Marlett and Park.[5h] They found that aluminum hydride–*N*,*N*-dimethylethylamine (AlH_3·NMe_2Et) in toluene reveals reducing characteristics essentially identical to those of aluminum hydride in THF.

In this study, we chose aluminum hydride–triethylamine complex (AHTEA) as representative of the aluminum hydride–amine complexes. Because the solution of AHTEA in THF is stable at room temperature, we decided to examine the reducing characteristics of the reagent toward the standard organic functionalities under practical conditions (THF, room temperature, the calculated amount of reagent to compound).

Results and Discussion

Preparation of Aluminum Hydride Solutions. As pointed out earlier, aluminum hydride is commonly prepared by adding a theoretical quantity of 100% sulfuric acid to lithium aluminum hydride in THF solution, as in eq 1. However, there has been a need for more convenient preparation of the aluminum hydride solutions.

† H. C. Brown and R. B. Wetherill Laboratories of Chemistry, Purdue University, West Lafayette, IN 47907.

(1) Some examples: (a) Ellefson, C. R.; Cusic, J. W. *J. Med. Chem.* **1976**, *19*, 1345. (b) Martinez, E.; Muchowski, J. M.; Velarde, E. *J. Org. Chem.* **1977**, *42*, 1087. (c) Packer, R. A.; Whitehurst, J. S. *J. Chem. Soc., Perkin Trans. 1* **1978**, 110. (d) Jacob, P., III; Kline, T.; Castagnoli, N., Jr. *J. Med. Chem.* **1979**, *22*, 662. (e) Martin, S. F.; Williamson, S. A.; Gist, R. P.; Smith, K. M. *J. Org. Chem.* **1983**, *48*, 5170. (f) Pratt, J. A. E.; Sutherland, I. O.; Newton, R. F. *J. Chem. Soc., Perkin Trans. 1* **1988**, 13.

(2) Jorgenson, M. J. *Tetrahedron Lett.* **1962**, 559.

(3) (a) Brown, H. C.; Yoon, N. M. *J. Am. Chem. Soc.* **1966**, *88*, 1464. (b) Yoon, N. M.; Brown, H. C. *Ibid.* **1968**, *90*, 2927.

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(5) (a) Wiberg, E.; Nöth, H. *Z. Naturforsch.* **1955**, *10b*, 237. (b) Ruff, J. K.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1960**, *82*, 2141. (c) Davidson, J. M.; Wartik, T. *Ibid.* 5506. (d) Brown, H. C.; Singaram, B. *Inorg. Chem.* **1980**, *19*, 455. (e) Ehrlich, R.; Young, A. R.; Bernard, H.; Lichstein, M.; Perry, D. D. *Ibid.* **1963**, *2*, 650. (f) Peters, F. M. *Can. J. Chem.* **1964**, *42*, 1755. (g) Dilts, J. A.; Ashby, E. C. *Inorg. Chem.* **1970**, *4*, 855. (h) Marlett, E. M.; Park, W. S. *J. Org. Chem.* **1990**, *55*, 2968.

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It appears that methanesulfonic acid or hydrogen chloride could replace 100% sulfuric acid in the synthesis of aluminum hydride to avoid such difficulty (eqs 2 and 3). One problem is the solubility of lithium salts in THF.

$$LiAlH_4 + HCl\ (in\ Et_2O) \xrightarrow{THF} AlH_3 + LiCl + H_2\uparrow \quad (2)$$

$$LiAlH_4 + CH_3SO_3H \xrightarrow{THF} AlH_3 + CH_3SO_3Li + H_2\uparrow \quad (3)$$

Lithium chloride dissolves easily in THF to give solutions of ~1 M; lithium methanesulfate is less soluble, giving solutions of up to 0.11 M at 0 °C, the excess precipitating readily. If such an amount of dissolved salt in the THF does not affect the aluminum hydride reductions, the procedure in eq 3 would be quite convenient.

However, the use of sodium aluminum hydride instead of lithium aluminum hydride in the synthesis of aluminum hydride seems to be more desirable because of the lower cost of production and the lower solubility of the corresponding sodium salts formed as a byproduct. Sodium aluminum hydride reacts with methanesulfonic acid and hydrogen chloride in diethyl ether equally well (eqs 4 and 5).

$$NaAlH_4 + CH_3SO_3H \xrightarrow{THF} AlH_3 + CH_3SO_3Na\downarrow + H_2\uparrow \quad (4)$$

$$NaAlH_4 + HCl\ (in\ Et_2O) \xrightarrow{THF} AlH_3 + NaCl\downarrow + H_2\uparrow \quad (5)$$

The reaction of sodium aluminum hydride and methanesulfonic acid gives a gelatinous, voluminous precipitate, and the precipitate thus formed inhibits further reaction. Therefore, a sufficiently large stirring bar or a mechanical stirrer is required. In addition, the slurry *must* be centrifuged to recover the aluminum hydride solution. This procedure, therefore, is inconvenient, especially in making aluminum hydride in large quantity.

The reaction of sodium aluminum hydride and hydrogen chloride in diethyl ether (commercially available from Aldrich as 1.0 M solution[6]) gives an aluminum hydride solution in diethyl ether and THF with a fine solid of sodium chloride. The solid slowly settles upon standing. It is also readily removed by centrifugation. However, in practice, we do not need to remove the sodium chloride precipitate, which should not interfere with typical reductions and recovery procedures. In addition, the procedure of a mixed solvent of THF and diethyl ether should not cause any difficulty in typical reductions. However, in this study, we utilized pure aluminum hydride solutions in THF after distilling out diethyl ether.

Preparation of Aluminum Hydride–Triethylamine (AHTEA) Complex Solutions. In the present study, we have developed several methods to synthesize AHTEA complex utilizing sodium aluminum hydride, methanesulfonic acid, or hydrogen chloride in diethyl ether and triethylamine:[7] (1) addition of triethylamine to the aluminum hydride solution; (2) direct reaction of sodium aluminum hydride with methanesulfonic acid in the presence of amine; (3) direct reaction of sodium aluminum hydride with hydrogen chloride in diethyl ether in the presence of amine; and (4) reaction of sodium aluminum hydride with triethylamine hydrochloride in chloroform. Each procedure works equally well.

We utilized the aluminum hydride solution in THF thus prepared in the synthesis of the AHTEA solutions; the addition of 10% excess triethylamine to the aluminum hydride solution gives a pure AHTEA solution in THF (eq 6). The ^{27}Al NMR spectrum of the solution of AHTEA

$$AlH_3 + NEt_3 \xrightarrow{THF} \underset{AHTEA}{AlH_3{\cdot}NEt_3} \quad (6)$$

in THF showed a broad singlet at δ 136 ppm relative to $Al(H_2O)_6$.[2f] The pure AHTEA is a glassy liquid at room temperature, and the ^1H NMR spectrum in C_6H_6 showed 1:1 complex formation between aluminum hydride and triethylamine.[8]

The aluminum hydride solution in THF is slowly destroyed at room temperature,[3b] but AHTEA is stable in THF at room temperature for at least 1 month. However, under reflux, AHTEA also attacks THF slowly.

Alcohols, Phenols, Amines, and Thiols. The alcohols, phenols, and thiols examined all liberated hydrogen instantly and quantitatively in the reaction with a quantitative amount of AHTEA at room temperature. On the other hand, *n*-hexylamine liberated 1 equiv of hydrogen rapidly, but the second equiv was evolved relatively slowly to be complete in 3 h at room temperature. These results are summarized in Table I.

Aldehydes and Ketones. All of the aldehydes and ketones examined, with the exception of cinnamaldehyde, are cleanly reduced to the corresponding alcohols with a quantitative amount of hydride within 1 h at room temperature. In the case of cinnamaldehyde, the reagent in a theoretical amount needs a 6-h reaction time for completion, but 10% excess reagent accelerates the reaction to be complete within 3 h, providing the corresponding α,β-unsaturated alcohol in high yield. The results are summarized in Table II.

Quinones. Two examples for quinones were examined with 0.67 equiv of AHTEA (H^-/compd = 2) at room

Table I. Reaction of Aluminum Hydride–Triethylamine Complex with Representative "Active Hydrogen" Compounds in Tetrahydrofuran at Room Temperature[a]

compd	time	ratio of $AlH_3{\cdot}NEt_3$/compd	hydride used for hydrogen evln[b]
1-hexanol	5 min	0.33	1.01
benzyl alcohol	5 min	0.33	1.00
3-hexanol	5 min	0.33	1.00
3-ethyl-3-pentanol	5 min	0.33	1.00
phenol	5 min	0.33	0.99
n-hexylamine	0.25 h	0.67	1.85
	0.5 h	0.67	1.92
	1.0 h	0.67	1.95
	3.0 h	0.67	1.99
1-hexanethiol	5 min	0.33	0.99
benzenethiol	5 min	0.33	1.01

[a] 0.5 *M* of the reagent in THF and 1.0 *M* of the compounds examined in THF were utilized for reactions. [b] Mmoles of hydride per mmol of compound.

(6) The use of ~3 M hydrogen chloride in diethyl ether, which was prepared from hydrochloric acid and sulfuric acid using an automatic gasimeter,[9] works equally well.

(7) These methods are also applicable for preparation of a general class of aluminum hydride–trialkylamine complexes.

(8) ^1H NMR (C_6H_6): δ 3.8 (s, 3H, AlH_3), 2.3 (q, 6H, NCH_2CH_3), 0.8 (t, 9H, NCH_2CH_3).

(9) Brown, H. C.; Kramer, G. W.; Levy, A. B.; Midland, M. M. *Organic Synthesis via Boranes*; Wiley-Interscience: New York, 1975.

Table II. Reaction of Aluminum Hydride–Triethylamine Complex with Representative Aldehydes and Ketones in Tetrahydrofuran at Room Temperature[a]

compd	time, h	ratio of AlH_3·NEt_3/compd	hydride used for redn	product	yield,[c] %
caproaldehyde	0.5	0.33	0.99	1-hexanol	98.5
benzaldehyde	0.5	0.33	1.00	benzyl alcohol	100
2-heptanone	0.5	0.33	1.01	2-heptanol	100
norcamphor	0.5	0.33	0.99	norborneol	100[d]
acetophenone	1.0	0.33	1.00	1-phenylethanol	94
benzophenone	1.0	0.33	1.00	benzhydrol	100
cinnamaldehyde	6.0	0.33	1.01		
	3.0	0.36	1.00	cinnamyl alcohol	97

[a,b] See corresponding footnotes in Table I. [c] GC yields. [d] *exo:endo* = 2.5:97.5.

Table III. Reaction of Aluminum Hydride–Triethylamine Complex with Representative Quinones in Tetrahydrofuran at Room Temperature[a]

compd	time, h	ratio of AlH_3·NEt_3/compd	hydride used for hydrogen evln[b]	hydride used for redn[b]
p-benzoquinone	3.0	0.67	0.70	1.29[c]
anthraquinone	6.0	0.67	0.49	1.50[d]

[a,b] See corresponding footnotes in Table I. [c] Along with 0.70 equiv of hydrogen evolution. [d] Along with 0.49 equiv of hydrogen evolution.

temperature. The reaction of *p*-benzoquinone slowly utilized 2 equiv of hydride per mol of compound of which 35% was for hydrogen evolution and the remaining 65% for reduction, whereas anthraquinone consumed 2 equiv of hydride, of which 25% was for hydrogen evolution and 75% for reduction. These values indicate that the reduction of *p*-benzoquinone proceeded to give 70% of hydroquinone and 30% of 1,4-dihydroxycyclohexadiene, whereas anthraquinone was reduced to give a 50:50 distribution ratio between hydroquinone and anthracenediol.[10] The experimental data are summarized in Table III.

Carboxylic Acids and Derivatives. Carboxylic acids and their derivatives were examined with a theoretical amount of the reagent at room temperature. The acids were reduced readily to the corresponding alcohols after immediate evolution of 1 equiv of hydrogen. Acid anhydrides also underwent quantitative reduction to the corresponding diols in 6 h. 10% excess reagent accelerated the reaction to be complete in 3 h. Acid chlorides were reduced rapidly and cleanly to the corresponding alcohols. The results are summarized in Table IV.

Esters and Lactones. The reactions of esters and lactones, except for acetates, with 0.67 equiv of the reagent formed a white voluminous precipitate immediately and proceeded slowly, requiring an extended reaction time for complete reduction. These slow reactions seem to be due to the presence of active hydrides in the precipitate. However, excess reagent (H^-/compd = 3) reduced both esters and lactones rapidly to the corresponding alcohols within 0.5 h at room temperature. On the other hand, the acetates were reduced rapidly with a quantitative amount of AHTEA without using excess reagent. These results are summarized in Table V.

Epoxides. The results of reducing four epoxides are summarized in Table VI. All of the aliphatic epoxides examined were rapidly reduced with a quantitative amount of AHTEA to give the S_N2-type of ring-opened products exclusively, whereas the reaction of styrene oxide, an aromatic one, proceeded slowly to afford a mixture of 77% 1-phenylethanol and 23% 2-phenylethanol.

Amides and Nitriles. Primary amides with 1.33 equiv of the reagent (H^-/compd = 4) liberated 2 equiv of hydrogen rapidly, but the reduction proceeded very slowly. However, excess reagent (H^-/compd = 6) reduced primary amides relatively fast to the corresponding amines in high yields. On the other hand, the reductions of tertiary amides with a theoretical amount of the reagent (H^-/compd = 2) were rapid, the uptake of 2 equiv of hydride being complete in less than 0.5 h, providing the corresponding tertiary amines in high yields.

Both capronitrile and benzonitrile utilized 2 equiv of hydride rapidly to be reduced cleanly to the corresponding amines. In these cases, no hydrogen evolution was noted. Furthermore, nitriles possessing acidic α-protons are also reduced readily to the corresponding amines without evolution of a significant amount of hydrogen. The results are summarized in Table VII.

Nitro Compounds and Their Derivatives. 1-Nitropropane readily consumed a total of 5 equiv of hydride with 2.5 equiv of hydride being utilized for hydrogen evolution and 2.5 equiv for reduction, corresponding to the 1,2-dialkylhydrazine stage. Nitrobenzene was also reduced to hydrazobenzene, but only slowly. Similarly, the reactions of azobenzene and azoxybenzene with a theoretical amount of the reagent proceeded very slowly and incompletely, but with excess reagent, they underwent reduction slowly to the hydrazobenzene stage in 5 days. The experimental data are summarized in Table VIII.

Other Nitrogen Compounds. The reaction of cyclohexanone oxime with 1.33 equiv of the reagent rapidly liberated *ca.* 1.4 equiv of hydrogen and utilized 2 equiv of hydride for reduction, corresponding to the formation of cyclohexylamine. The amount of hydrogen evolved was not changed significantly, even using excess reagent (H^-/compound = 6), but the reduction was complete rapidly in 0.5 h at room temperature. Phenyl isocyanate was also readily reduced to *N*-methylaniline in a high yield. The double bonds in hetero aromatic ring compounds, such as pyridine and 4-picoline *N*-oxide, were slowly attacked by this reagent. These results are summarized in Table IX.

Sulfur Compounds. Diphenyl disulfide was reduced readily by a theoretical amount of AHTEA to the thiol with evolution of 1 equiv of hydrogen, whereas di-*n*-butyl disulfide was reduced only slowly. In this case, excess reagent and an extended reaction time were needed for complete reduction; 1 equiv of AHTEA reduced the disulfide slowly, but completely, yielding 2 equiv of 1-butanethiol in 24 h at room temperature. Sulfoxides, such as dimethyl sulfoxide, are also readily reduced to the corresponding sulfides. On the other hand, sulfides,

(10) Brown, H. C.; Weissman, P. M.; Yoon, N. M. *J. Am. Chem. Soc.* **1966**, *88*, 1458.
(11) GC analysis showed the solution contains *ca.* 90% THF and *ca.* 10% diethyl ether.

Table IV. Reaction of Aluminum Hydride–Triethylamine Complex with Representative Carboxylic Acids and Derivatives in Tetrahydrofuran at Room Temperature[a]

compd	time, h	ratio of AlH_3·NEt_3/compd	hydride used for redn	product	yield,[c] %
benzoic acid	3.0	1.00	2.00[d]	benzyl alcohol	98
caproic acid	1.0	1.00	1.99[d]	1-hexanol	99
acetic anhydride	0.5	1.33	4.01		
succinic anhydride	6.0	1.33	3.97		
	3.0	1.46	3.99		
phthalic anhydride	6.0	1.33	3.97	*o*-xylene-α,α'-diol	92[e]
	3.0	1.46	3.99		
caproyl chloride	0.5	0.67	2.01	1-hexanol	99.5
benzoyl chloride	0.5	0.67	2.00	benzyl alcohol	99

[a,b] See corresponding footnotes in Table I. [c] GC yields. [d] Along with 1 equiv of hydrogen evolution. [e] An isolated yield.

Table V. Reaction of Aluminum Hydride–Triethylamine Complex with Representative Esters and Lactones in Tetrahydrofuran at Room Temperature[a]

compd	time, h	ratio of AlH_3·NEt_3/compd	hydride used for redn[b]	product	yield,[c] %
ethyl caproate	12.0	0.67	1.94		
	12.0	0.74	1.99[d]		
	0.25	1.00	2.00	1-hexanol	99.5
ethyl benzoate	12.0	0.67	1.93		
	12.0	0.74	1.97		
	0.5	1.00	2.01	benzyl alcohol	98.5
phenyl acetate	0.25	0.67	2.00		
γ-butyrolactone	6.0	0.67	1.33		
	0.5	1.00	1.99		
phthalide	3.0	0.67	1.32		
	0.25	1.00	2.01	*o*-xylene-α,α'-diol	87[d]
isopropenyl acetate	0.25	0.67	1.99		

[a,b] See corresponding footnotes in Table I. [c] GC yields. [d] An isolated yield.

Table VI. Reaction of Aluminum Hydride–Triethylamine Complex with Representative Epoxides in Tetrahydrofuran at Room Temperature[a]

compd	time, h	ratio of AlH_3·NEt_3/compd	hydride used for redn[b]	product	yield,[c] %
1,2-butylene oxide	0.5	0.33	1.01	2-butanol	100[d]
styrene oxide	6.0	0.33	1.00	1-phenylethanol	77
				2-phenylethanol	23
cyclohexene oxide	0.5	0.33	1.01	cyclohexanol	99
1-methyl-1,2-cyclohexene oxide	0.5	0.33	1.01	1-methylcyclohexanol	99.5[d]

[a,b] See corresponding footnotes in Table I. [c] GC yields. [d] No isomers detected.

Table VII. Reaction of Aluminum Hydride–Triethylamine Complex with Representative Amides and Nitriles in Tetrahydrofuran at Room Temperature[a]

compd	time, h	ratio of AlH_3·NEt_3/compd	hydride used for redn[b]	product	yield,[c] %
caproamide	72.0	1.33	1.45[d]		
	48.0	2.00	1.99[d]	hexylamine	93
benzamide	72.0	1.33	1.32[d]		
	48.0	2.00	2.01[d]	benzylamine	94
N,N-dimethylcaproamide	0.5	0.67	2.01	*N,N*-dimethylhexylamine	97
N,N-dimethylbenzamide	0.5	0.67	1.99	*N,N*-dimethylbenzylamine	96
capronitrile	0.5	0.67	1.99	hexylamine	96.5
benzonitrile	0.5	0.67	1.99	benzylamine	98
diphenylacetonitrile	1.0	1.00	2.01[e]	2,2-diphenylethylamine	98.5 (92)[f]
phenylacetonitrile	1.0	1.00	2.01	α-methylbenzylamine	96.5
3-butenenitrile	3.0	0.67	1.97		
	1.0	1.00	2.01	3-butenylamine	92.5

[a,b] See corresponding footnotes in Table I. [c] Yields estimated by titration. [d] Along with 2 equiv of hydrogen evolution. [e] Along with 0.09 equiv of hydrogen evolution. [f] An isolated yield.

sulfones, and other sulfur compounds examined are essentially inert to this reagent. These results are summarized in Table X.

Conclusion

The reducing power of aluminum hydride–triethylamine (AHTEA) complex in tetrahydrofuran toward 59 selected organic compounds containing representative functional groups under practical conditions (tetrahydrofuran, room temperature, the quantitative amount of reagent to compound) has been investigated. In this way, we have established that quantitative reduction of various organic functionalities can be readily achieved using the calculated quantity of AHTEA to avoid the use of reagent. This permits ready use of the aluminum hydride reagent in organic synthesis with high convenience and efficiency, with the possibility of an improved selectivity than that of aluminum hydride itself in tetrahydrofuran.

Experimental Section

All glassware used in the experiments was predried thoroughly in a drying oven and cooled under a dry nitrogen atmosphere. Hypodermic syringes were used to transfer solutions. All

Table VIII. Reaction of Aluminum Hydride–Triethylamine Complex with Representative Nitro Compounds and Their Derivatives in Tetrahydrofuran at Room Temperature[a]

compd	time, h	ratio of AlH_3·NEt_3/compd	hydride used for redn[b]	product	yield,[c] %
1-nitropropane	3.0	2.00	2.52[d]		
nitrobenzene	96.0	2.00	2.61[d]	1,2-diphenylhydrazine	93
azobenzene	120.00	0.67	0.78		
	96.0	1.33	1.11[e]	1,2-diphenylhydrazine	91
azoxybenzene	72.0	1.33	1.39		
	120.0	2.00	2.12[f]	1,2-diphenylhydrazine	89

[a,b] See corresponding footnotes in Table I. [c] Isolated yields. [d] Along with 2.5 equiv of hydrogen evolution. [e] Along with 1.02 equiv of hydrogen evolution. [f] Along with 1.87 equiv of hydrogen evolution.

Table IX. Reaction of Aluminum Hydride–Triethylamine Complex with Other Nitrogen Compounds in Tetrahydrofuran at Room Temperature[a]

compd	time, h	ratio of AlH_3·NEt_3/compd	hydride used for redn	product	yield,[c] %
cyclohexanone oxime	3.0	1.33	1.99[e]		
	0.5	2.00	2.01[f]	cyclohexylamine	94[d]
phenyl isocyanate	3.0	1.00	3.01	*N*-methylaniline	98
pyridine	3.0	1.00	1.05		
	24.0	1.00	1.71		
	48.0	1.00	2.04		
4-picoline *N*-oxide	3.0	1.33	2.13		
	24.0	1.33	2.40		
	48.0	1.33	2.58[g]		

[a,b] See corresponding footnotes in Table I. [c] GC yield. [d] A yield estimated by titration. [e] Along with 1.39 equiv of hydrogen evolution. [f] Along with 1.46 equiv of hydrogen evolution. [g] Along with 0.78 equiv of hydrogen evolution.

Table X. Reaction of Aluminum Hydride–Triethylamine Complex with Representative Sulfur Compounds in Tetrahydrofuran at Room Temperature[a]

compd	time, h	ratio of AlH_3·NEt_3/compd	hydride used for redn[b]	product	yield,[c] %
di-*n*-butyl disulfide	24.0	0.67	0.44[d]		
	24.0	1.00	1.05[e]	1-butanethiol	96.5[d]
diphenyl disulfide	3.0	0.67	1.01[f]	benzenethiol	97
	0.5	1.00	1.00[f]		
phenyl *n*-propyl sulfide	3.0	0.33	0.00		
dimethyl sulfoxide	1.0	0.67	0.99		
diphenyl sulfone	3.0	0.67	0.00		
methanesulfonic acid	6.0	1.33	0.00[f]		
p-toluenesulfonic acid monohydrate	6.0	1.33	0.01[g]		
cyclohexyl tosylate	48.0	1.00	0.03[h]	cyclohexene	41
				cyclohexane	1

[a,b] See corresponding footnotes in Table I. [c] GC yield. [d] Along with 0.31 equiv of hydrogen evolution. [e] Along with 0.59 equiv of hydrogen evolution. [f] Along with 1 equiv of hydrogen evolution. [g] Three equiv of hydrogen evolved immediately. [h] Along with 0.43 equiv of hydrogen evolution.

reactions were carried out under a static pressure of nitrogen in flasks fitted with septum-covered sidearms with use of standard techniques for handling air-sensitive materials.[10]

Materials. 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. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl and stored under dry nitrogen. Sodium aluminum hydride was obtained from the Ethyl Corp. and used directly without further purification. Hydrogen chloride in diethyl ether was purchased from the Aldrich Chemical Co. or synthesized from hydrochloric acid and sulfuric acid using an automatic gasimeter.[9]

Instruments. GC analyses were carried out on a Varian Model 5730A FID chromatograph equipped with a Hewlett-Packard 3390A integrator/plotter. All GC yields were determined with use of a suitable internal standard and authentic mixtures. NMR spectrometers used were a Varian Model T-60 (60 MHz) for ^1H NMR spectrum and a Varian FT-80A for ^{27}Al NMR spectrum.

Preparation of Sodium Aluminum Hydride in Tetrahydrofuran. An oven-dried, 2-L, round-bottom flask with sidearm, equipped with a magnetic stirring bar and an adapter, was attached to a mercury bubbler. The flask was flushed with dry nitrogen and then maintained under a static pressure of nitrogen. The flask was charged with *ca.* 40 g of sodium aluminum hydride (*ca.* 750 mmol) and 600 mL of THF. The slurry was stirred for at least 48 h at room temperature and then allowed to stand at 0 °C to permit the undissolved materials to settle. The ^{27}Al NMR spectrum of the resulting clear solution showed a clean quintet centered at δ 96.7 (relative to $Al(H_2O)_6^{3+}$) (J_{Al-H} = 175 Hz). The concentration of sodium aluminum hydride in THF measured by hydrolysis was 1.2 M. This solution was used for further reactions.

Preparation of Aluminum Hydride in Tetrahydrofuran. By means of a double-ended needle and a mass cylinder, 500 mL of 1.2 M sodium aluminum hydride thus prepared was introduced into a 2-L flask, fitted with an inlet port and magnetic stirring bar and connected to a gas meter *via* the reflux condenser. The solution was cooled to 0 °C, and precooled 600 mL of 1.0 M hydrogen chloride (600 mmol) in diethyl ether was added slowly with vigorous stirring. There was evolved *ca.* 610 mmol of hydrogen. The solution was permitted to stir for 1 h and then allowed to stand at 0 °C to permit the sodium chloride precipitate to settle. The clear supernatant solution was removed by a syringe, and diethyl ether was distilled from the solution using an aspirator until the volume of solution reduced by half. The ^{27}Al NMR spectrum of the solution showed a broad singlet centered at δ 126 (relative to $Al(H_2O)_6^{3+}$). The concentration of aluminum hydride in THF[12] was 0.52 M. This solution was used for further reactions.

(12) For practical purposes, a simple procedure for the preparation of AHTEA solution was developed. The sodium aluminum hydride solution in THF was treated with the calculated amount of 3 M hydrogen chloride in diethyl ether. This aluminum hydride solution in a mixed solvent of THF and diethyl ether in the presence of sodium chloride was directly used for further reaction with triethylamine to prepare AHTEA. The solution of AHTEA in the mixed solvent in the presence of sodium chloride showed essentially the same reductions.

Preparation of Aluminum Hydride–Triethylamine (AHTEA) Complex in Tetrahydrofuran.[12] To 400 mL of 0.52 M aluminum hydride in THF (208 mmol), thus prepared was added 23.2 g of triethylamine (229 mmol). The concentration of the solution was 0.50 M. The ^{27}Al NMR spectrum of AHTEA in THF showed a broad singlet at δ 136 relative to $Al(H_2O)_6^{3+}$. The pure AHTEA, after evaporation of all volatile materials, is a glassy liquid at room temperature and the ^1H NMR spectrum in C_6H_6 showed a clean 1:1 complex.[8]

A solution of 0.50 M in aluminum hydride–triethylamine was stored under nitrogen for 1 month at room temperature, and aliquots were removed for analysis. There was not observed any change in concentration. However, under reflux, there were observed changes from 0.50 to 0.45 M in 1 day to 0.35 M in 2 days and to 0.28 M in 3 days.

General Procedure Used for Hydride Reductions. The following procedure was used for quantitative studies. The reduction of benzoic acid is described as an example of the experimental procedure. The AHTEA solution, 20.0 mL of 0.50 M (10.0 mmol of the reagent, 30.0 mmol of hydride), was introduced into a dried, 100-mL flask fitted with a rubber syringe cap on an inlet port, a magnetic stirring bar, and a bent adapter connected to a gas buret through a reflux condenser and a dry ice vapor trap. The flask was immersed in a water bath, the stirred solution was brought to room temperature, and 1.22 g of benzoic acid (10.0 mmol) in 10 mL of THF was injected slowly. One equiv of hydrogen was evolved instantly. After 30 min, a 4.0-mL aliquot of the reaction mixture was removed and injected into a 10% sulfuric acid solution to measure residual hydride. The hydrogen evolved amounted to 0.24 mmol, which indicates that 1.76 mmol of hydride was used for reduction per mmol of compound. Aliquots were also removed and hydrolyzed after 1.0 and 3.0 h of the reaction time. After 3 h, there was not observed any active hydride remaining in the reaction mixture. Obviously, the reaction was complete in 3.0 h.

To determine the reduction product, 15 mL of the reaction mixture was removed and treated with 10% sulfuric acid. Hexadecane (1.13 g, 5.0 mmol) was added as an internal standard. The gas chromatographic analysis with use of a 12-ft × 0.125-in. column of 10% Carbowax 20M on 100–200-mesh Supelcoport showed 98% benzyl alcohol.

Estimation of Amines by Titration. The reduction of *N,N*-dimethylcaproamide is described as representative. In the usual setup, 1.43 g of *N,N*-dimethylcaproamide (10.0 mmol) was reduced with 13.4 mL of AHTEA (0.5 M, 6.7 mmol) for 0.5 h at room temperature. After this, the reaction mixture was hydrolyzed with 5 mL of water and 1 g of sodium hydroxide pellets. The clear solution was decanted and the residue was extracted with diethyl ether twice. The combined extract was diluted to 100 mL. To 5 mL of the amine solution was added 5.0 mL of 0.1 *N* HCl. This was thoroughly shaken and titrated with 0.05 *N* sodium carbonate using methyl red as an indicator. Two titrations were carried out for the determination of each amine; 2.60 and 2.65 mL of 0.05 *N* sodium carbonate were needed, which correspond to 98 and 96.5% yields of amine after correction for the presence of triethylamine.

Isolation of Products. The following reduction of phthalide is representative. To 20 mmol of AHTEA in 40 mL of THF solution was added 2.68 g of phthalide (20 mmol) in 20 mL of THF at room temperature. After 15 min, the reaction mixture was hydrolyzed with 10% sulfuric acid. The aqueous layer was then saturated with potassium carbonate and thoroughly extracted with THF. The combined THF extract was dried over anhydrous sodium sulfate. After solvents were removed under reduced pressure, there was obtained *o*-xylene-α,α'-diol, a light yellowish solid: 2.40 g (87% yield), mp 62–64 °C [lit.[13] 63–65 °C]. The product was further confirmed by ^1H NMR.

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