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Reaction of Bis(diethylamino)aluminum Hydride in Tetrahydrofuran with Selected Organic Compounds Containing Representative Functional Groups

Jin Soon Cha*, Oh Oun Kwon, and Jong Mi Kim

Department of Chemistry, Yeungnam University, Kyongsan 712-749

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Bis(diethylamino)aluminum hydride was utilized in a systematic study of the approximate rates and stoichiometry of the reaction of excess reagent with 55 selected organic compounds containing representative functional groups under standardized conditions (THF, 0℃, reagent to compound = 4 : 1) in order to define the characteristics of the reagent for selective reductions. The reducing action of BEAH was also compared with that of the parent aluminum hydride. The reducing action of the reagent is quite similar to that of aluminum hydride, but the reducing power is much weaker. Aldehydes and ketones were readily reduced in 1-3 h to the corresponding alcohols. However, unexpectedly, a ready involvement of the double bond in cinnamaldehyde was realized to afford hydrocinnamyl alcohol. The introduction of diethylamino group to the parent aluminum hydride appears not to be appreciably influential in stereoselectivity on the reduction of cyclic ketones. Both *p*-benzoquinone and anthraquinone utilized 2 equiv of hydride readily without evolution of hydrogen, proceeded cleanly to the 1,4-reduction products. Carboxylic acids and acid chlorides underwent reduction to alcohols slowly, whereas cyclic anhydrides utilized only 2 equiv of hydride slowly to the corresponding hydroxylacids. Especially, benzoic acid with a limiting amount of hydride was reduced to benzaldehyde in a yield of 80%. Esters and lactones were also readily reduced to alcohols. Epoxides examined all reacted slowly to give the ring-opened products. Primary and tertiary amides utilized 1 equiv of hydride fast and further hydride utilization was quite slow. The examination for possibility of achieving a partial reduction to aldehydes was also performed. Among them, benzamide and N,N-dimethylbenzamide gave *ca.* 90% yields of benzaldehyde. Both the nitriles examined were also slowly reduced to the amines. Unexpectedly, both aliphatic and aromatic nitro compounds proved to be relatively reactive to the reagent. On the other hand, azo- and azoxybenzenes were quite inert to BEAH. Cyclohexanone oxime liberated 1 equiv of hydrogen and utilized 1 equiv of hydride for reduction, corresponding to *N*-hydroxycyclohexylamine. Pyridine ring compounds were also slowly attacked. Disulfides were readily reduced with hydrogen evolution to the thiols, and dimethyl sulfoxide and diphenyl sulfone were also rapidly reduced to the sulfides.

Introduction

The dialkylamino-substituted derivatives of lithium aluminum hydride have appeared to exhibit reducing properties significantly different from those of the parent reagent.[1] For example, lithium tris(diethylamino)aluminum hydride (LTDEA) has proven to be a valuable selective reducing agent for transformation of carboxylic acids,[2] esters,[3,4] primary carboxamides,[4,5] tertiary carboxamides[4,6] and aromatic nitriles[4,7] to the corresponding aldehydes.

Similarly, the dialkylaminoaluminum hydrides are expected to exhibit reducing properties different from those of the parent reagent. In fact, as Mukaiyama and coworker first reported in 1970s, the dialkylaminoaluminum hydrides were shown to reduce carboxylic acids and esters to aldehydes in good yields.[8,9] Accordingly, it appeared desirable to undertake a systematic exploration of the reaction of bis(diethylamino)aluminum hydride (BEAH), one of the class of dialkylamino derivatives, with organic compounds containing representative functional groups, under standardized conditions in order to define its reducing characteristics. The reducing properties of BEAH are also compared to those of the parent aluminum hydride.

Results and Discussion

The usual laboratory procedure for preparation of dialkylaminoaluminum hydrides involves the reaction of lithium aluminum hydride and dialkylammonium chlorides,[10] or aluminum hydride (prepared from lithium aluminum hydride) with dialkylamines[11,12] Eq. (1). The use of this method seems to be

$$LiAlH_4 \rightarrow AlH_3 \xrightarrow{2\ R_2NH} HAl(NR_2)_2 + 2\ H_2\uparrow \qquad (1)$$

limited by the high cost of the reagents. Ashby and coworker also reported the economical synthesis of dialkylaminoaluminum hydrides by the reaction of aluminum, hydrogen, and a secondary amine at moderate temperature and pressure[13]; however, the procedure appears to be inconvenient in laboratory use.

Very recently, we reported that the use of sodium aluminum hydride instead of lithium aluminum hydride in the synthesis of aluminum hydride provides a convenient and economical method because of the lower cost of production and the lower solubility of the corresponding sodium salts formed as a by-product.[14] Sodium aluminum hydride reacts with methanesulfonic acid or hydrogen chloride in diethyl ether to afford aluminum hydride in a pure form Eq. (2)-(3). Therefore, various dialkylaminoaluminum

$$NaAlH_4 + CH_3SO_3H \xrightarrow{THF} AlH_3 + CH_3SO_3Na\downarrow + H_2\uparrow \qquad (2)$$

$$NaAlH_4 + HCl(\text{in } Et_2O) \xrightarrow{THF} AlH_3 + NaCl\downarrow + H_2\uparrow \qquad (3)$$

hydrides can be conveniently prepared from the reaction of aluminum hydride and the corresponding dialkylamines.

Alcohols, phenols, amines, and thiols (active hydrogen compound). There is no discrimination in the rate of hydrogen evolution among alcohols examined: the alcohols and phenols examined all liberated hydrogen slowly in 1-3 h at 0℃. The reaction of thiols with the reagent evoled hydrogen slower than that of alcohols, showing the complete hydrogen evolution in 6-12 h. On the other hand, *n*-hexylamine liberated only 1 equiv of hydrogen rapidly, with the second being evolved only slowly. The results are summarized in Table 1.

The parent aluminum hydride reacted with all the alcohols, phenols and thiols examined to evolve hydrogen instantly and quantitatively.[15] On the other hand, like the case of BEAH, the reaction of *n*-hexylamine with aluminum hydride liberated 1 equiv of hydrogen rapidly, with the second being evolved slowly.[15]

Aldehydes and ketones. All of the saturated aldehydes and ketones examined utilized 1 equiv of hydride readily in 1-3 h to produce the corresponding alcohols, but the rate of reaction was much slower than aluminum hydride.[15] The reaction of cinnamaldehyde, an α,β-unsaturated aldehyde, showed an unexpected result: a ready involvement of the double bond to afford hydrocinnamyl alcohol. This is a contrast to the case of aluminum hydride. The reaction of cinnamaldehyde with aluminum hydride utilized immediately 1 equiv of hydride and no further hydride uptake was realized. These results are summarized in Table 2.

The stereoselectivity of BEAH in the reduction of cyclic ketones is listed and compared to that of aluminum hydride in Table 3. The introduction of diethylamino group to the parent aluminum hydride appears not to be appreciably influential in stereoselectivity.

Table 1. Reaction of Bis(diethylamino)aluminum Hydride with Representative Active Hydrogen Compounds in Tetrahydrofuran at 0℃

Compound[a]	Time, h	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
1-Hexanol	0.25	0.90	0.90	0.00
	0.5	0.93	0.93	0.00
	1.0	1.00	1.00	0.00
Benzyl alcohol	0.25	0.92	0.92	0.00
	0.5	0.95	0.95	0.00
	1.0	1.00	1.00	0.00
3-Hexanol	0.25	0.91	0.91	0.00
	0.5	0.94	0.94	0.00
	1.0	1.00	1.00	0.00
3-Ethyl-3-pentanol	0.25	0.87	0.87	0.00
	0.5	0.91	0.91	0.00
	1.0	0.99	0.99	0.00
	3.0	1.01	1.01	0.00
Phenol	0.25	0.89	0.89	0.00
	0.5	0.92	0.92	0.00
	1.0	0.98	0.98	0.00
	3.0	1.01	1.01	0.00
n-Hexylamine	0.25	0.85	0.86	0.01
	0.5	1.18	1.19	0.01
	3.0	1.49	1.50	0.01
	12.0	1.52	1.53	0.01
	24.0	1.60	1.61	0.01
	48.0	1.89	1.90	0.01
	72.0	1.98	1.99	0.01
1-Hexanethiol	0.25	0.49	0.49	0.00
	0.5	0.67	0.67	0.00
	1.0	0.80	0.80	0.00
	3.0	0.95	0.95	0.00
	6.0	0.98	0.98	0.00
	12.0	0.99	0.99	0.00
Benzenthiol	0.25	0.61	0.61	0.00
	0.5	0.70	0.70	0.00
	1.0	0.83	0.83	0.00
	3.0	0.98	0.98	0.00
	6.0	1.00	1.00	0.00

[a] 10.0 mmol of compound was added to 40.0 mmol of the reagent (1.0 M in reagent and 0.25 M in compound). [b] Mmol per a mmol of compound.

Quinones. As was pointed out earlier[15], the reduction of a quinone to hydroquinone should utilize 2 equiv of hydride, 1 for reduction and 1 for hydrogen evolution. On the other hand, the reduction of the quinone to the 1,4-dihydroxycyclohexadiene stage should require 2 equiv of hydride for reduction, without hydrogen evolution. On this basis, the reaction of *p*-benzoquinone and anthraquinone with BEAH, which utilized 2 equiv of hydride readily without hydrogen evolution, proceeded cleanly to the 1,4-reduction products, 1,4-dihydroxycyclohexadiene and 9,10-dihydro-9,10-anthrace-

Table 2. Reaction of Bis(diethylamino)aluminum Hydride with Representative Aldehydes and Ketones in Tetrahydrofuran at 0℃

Compound[a]	Time, h	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Caproaldehyde	0.25	0.02	0.89	0.87
	0.5	0.02	0.97	0.95
	1.0	0.02	1.02	1.00
Benzaldehyde	0.25	0.04	0.94	0.90
	0.5	0.04	1.03	0.99
	1.0	0.04	1.04	1.00
2-Heptanone	0.25	0.00	0.87	0.87
	0.5	0.00	0.92	0.92
	1.0	0.00	0.98	0.98
	3.0	0.00	1.01	1.01
Norcamphor	0.25	0.01	0.89	0.88
	0.5	0.01	0.92	0.91
	1.0	0.01	0.97	0.96
	3.0	0.01	1.01	1.00
Acetophenone	0.25	0.00	0.91	0.91
	0.5	0.00	0.95	0.95
	1.0	0.00	0.97	0.97
	3.0	0.00	1.00	1.00
Benzophenone	0.25	0.00	0.92	0.92
	0.5	0.00	0.98	0.98
	1.0	0.00	1.00	1.00
Cinnamaldehyde[c]	0.25	0.00	1.53	1.53
	0.5	0.00	1.87	1.87
	3.0	0.00	1.96	1.96
	12.0	0.00	1.99	1.99

[a,b]See the corresponding footnotes in Table 1. [c]Solution changed from colorless to yellow.

Table 3. Stereochemistry in the Reduction of Cyclic Ketones with Bis(diethylamino)-aluminum Hydride and Aluminum Hydride in Tetrahydrofuran at 0℃

Compound	Less stable isomer (%)[a,b]	
	AlH_3[c]	$(Et_2N)_2AlH$
Cyclohexanone		
2-methyl-	26	51
3-methyl-	–	31
4-methyl-	–	41
4-*t*-butyl-	13	21
3,3,5-trimethyl-	88	88
Norcamphor	93	94
Camphor	90	83

[a]Excess reagent utilized, [b]Quantitative yields of alcohols, [c]Data taken from ref. 15.

Table 4. Reaction of Bis(diethylamino)aluminum Hydride with Representative Quinones in Tetrahydrofuran at 0℃

Compound[a]	Time, h	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
p-Benzoquinone[c,d]	0.25	0.00	1.04	1.04
	0.5	0.04	1.25	1.21
	1.0	0.04	1.53	1.49
	3.0	0.04	1.77	1.73
	6.0	0.04	2.06	2.02
Anthraquinone[c,e]	0.25	0.00	1.19	1.19
	0.5	0.00	1.34	1.34
	1.0	0.00	1.57	1.57
	3.0	0.00	1.88	1.88
	6.0	0.00	2.01	2.01

[a,b]See corresponding footnotes in Table 1. [c]Batch reaction. [d]Dark precipitate formed. [e]Reverse addition; color changed into yellow.

nediol, respectively.

On the other hand, the reduction of *p*-benzoquinone by aluminum hydride proceeded to give a 50 : 50 distribution between the two paths, whereas anthraquinone appeared to reduce cleanly to the 1,4-reduction product.[15] These results are summarized in Table 4.

Carboxylic acids and acyl derivatives. Carboxylic acids were reduced slowly to the corresponding alcohols with slow evolution of hydrogen. A careful examination of the rate and stoichiometry in the reaction of carboxylic acids suggests a possibility for aldehyde synthesis. In fact, a preliminary experiment showed that a 80% yield of benzaldehyde was obtained from the reaction of benzoic acid with BEAH in a limiting amount. Cyclic anhydrides utilized only 2 equiv of hydride slowly and further hydride consumption was very sluggish, suggesting the formation of hydroxylacids. On the other hand, acid chlorides underwent reduction to alcohols with ease, the reactions appearing to be complete in less than 3 h. Aluminum hydride reacted with all the carboxylic acids and acyl derivatives examined to give the corresponding alcohols with remarkable ease.[15] These results are summarized in Table 5.

Esters and lactones. Ethyl caproate and ethyl benzoate were reduced readily to the corresponding alcohols in 3-6 h. However, phenyl acetate and phthalide were slowly reduced to the alcohols. Unexpectedly, an exceptionally fast rate in the reaction or γ-butyrolactone was realized. Unlike these reactions, the reactions of esters and lactones with aluminum hydride were all completely reduced within 0.5 h. In similar to the case of aluminum hydride,[15] isopropenyl acetate utilized only 2 moles of hydride rapidly, with only a very slow incomplete reaction being evident thereafter. This suggests that the reduction proceeds to give an ethanol moiety and an aluminum derivative of the enol form of acetone which is relatively resistant to reduction. The experimental results are summarized in Table 6.

Epoxides. All the epoxides examined reacted slowly, the uptake of one hydride per mole of epoxide being essentially complete in 6 h at 0℃. The reaction of epoxides with this reagent is much slower than that with aluminum hydride.[15] The reaction with aluminum hydride was complete within 30 min at 0℃. The reduction of 1,2-butylene oxide

Table 5. Reaction of Bis(diethylamino)aluminum Hydride with Representative Carboxylic Acids and Acyl Derivatives in Tetrahydrofuran at 0℃

Compound[a]	Time, h	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Caproic acid	0.25	0.79	2.09	1.30
	1.0	0.88	2.39	1.51
	3.0	0.93	2.55	1.62
	6.0	0.99	2.70	1.71
	12.0	1.00	2.96	1.96
	24.0	1.00	3.00	2.00
Benzoic acid	0.25	0.85	2.19	1.34
	1.0	0.98	2.56	1.58
	3.0	1.00	2.69	1.69
	6.0	1.00	2.82	1.82
	12.0	1.00	3.00	2.00
Acetic anhydride[c]	0.25	0.02	1.25	1.23
	0.5	0.02	1.68	1.66
	3.0	0.02	2.41	2.39
	12.0	0.02	2.48	2.46
	72.0	0.02	2.80	2.78
Succinic anhydride[c,d]	0.25	0.00	1.49	1.49
	0.5	0.00	1.63	1.63
	3.0	0.00	1.92	1.92
	24.0	0.00	1.94	1.94
	72.0	0.00	2.08	2.08
Phthalic anhydride[c]	0.25	0.02	1.10	1.08
	0.5	0.02	1.25	1.23
	6.0	0.02	1.66	1.64
	24.0	0.02	1.80	1.78
	72.0	0.02	1.96	1.94
	120.0	0.02	2.05	2.03
Capropyl chloride	0.25	0.00	1.57	1.57
	0.5	0.00	1.85	1.85
	1.0	0.00	1.97	1.97
	3.0	0.00	2.01	2.01
Benzoyl chloride	0.25	0.00	1.80	1.80
	0.5	0.00	1.93	1.93
	1.0	0.00	2.00	2.00

[a,b] See corresponding footnotes in Table 1. [c] Hydride to compound = 6 : 1. [d] Solution changed to yellow.

Table 6. Reaction of Bis(diethylamino)aluminum Hydride with Representative Esters and Lactones in Tetrahydrofuran at 0℃

Compound[a]	Time, h	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Ethyl caproate	0.25	0.00	1.21	1.21
	0.5	0.00	1.54	1.54
	1.0	0.00	1.89	1.89
	3.0	0.00	1.99	1.99
	6.0	0.00	2.00	2.00
Ethyl benzoate	0.25	0.00	1.35	1.35
	0.5	0.00	1.51	1.51
	1.0	0.00	1.86	1.86
	3.0	0.00	2.01	2.01
Phenyl acetate	0.25	0.02	1.40	1.38
	1.0	0.02	1.67	1.65
	12.0	0.02	1.82	1.80
	24.0	0.02	1.85	1.83
	72.0	0.02	1.97	1.95
	96.0	0.02	2.01	1.99
γ-Butyrolactone	0.25	0.00	2.00	2.00
Phthalide[c]	0.25	0.00	1.23	1.23
	0.5	0.00	1.43	1.43
	3.0	0.00	1.79	1.79
	6.0	0.00	1.93	1.93
	24.0	0.00	1.97	1.97
	48.0	0.00	1.99	1.99
Isopropenyl acetate	0.25	0.03	2.01	1.98
	1.0	0.03	2.52	2.49
	12.0	0.03	2.56	2.53
	72.0	0.03	2.65	2.62

[a,b] See corresponding footnotes in Table 1. [c] Solution changed to yellow.

Table 7. Reaction of Bis(diethylamino)aluminum Hydride with Representative Epoxides in Tetrahydrofuran at 0℃

Compound[a]	Time, h	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
1,2-Butylene oxide	0.25	0.00	0.41	0.41
	0.5	0.00	0.60	0.60
	1.0	0.00	0.83	0.83
	3.0	0.00	0.92	0.92
	6.0	0.00	0.99	0.99
	12.0[c]	0.00	1.00	1.00
Cyclohexene oxide	0.25	0.02	0.40	0.38
	0.5	0.02	0.61	0.59
	1.0	0.02	0.84	0.82
	3.0	0.02	0.99	0.97
	6.0	0.02	1.01	0.99
Styrene oxide	0.25	0.00	0.80	0.80
	1.0	0.00	0.90	0.90
	3.0	0.00	0.96	0.96
	6.0	0.00	0.99	0.99
	12.0[d]	0.00	1.00	1.00

[a,b] See corresponding footnotes in Table 1. [c] A mixture of 92% 2-butanol and 8% 1-butanol formed. [d] A mixture of 5% 2- and 95% 1-phenylethanol.

gives 92% of 2-butanol and 8% of 1-butanol. However, aluminum hydride gives only 2-butanol, free of the other possible isomer. In the case of styrene oxide, BEAH gives a mixture of 5% 2- and 95% 1-phenylethanol. On the other hand, aluminum hydride shows more tendency to open at the more

Table 8. Reaction of Bis(diethylamino)aluminum Hydride with Representative Amides and Nitriles in Tetrahydrofuran at 0℃

Compound[a]	Time, h	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Caproamide	0.25	0.73	1.43	0.70
	0.5	0.75	1.56	0.81
	3.0	0.93	1.88	0.95
	6.0	0.98	1.96	0.98
	12.0	1.01	2.02	1.01
Benzamide	0.25	0.69	1.50	0.81
	0.5	0.79	1.69	0.90
	3.0	0.94	1.92	0.98
	6.0	0.99	1.99	1.00
N,N-Dimethyl-caproamide	0.25	0.00	1.53	1.53
	0.5	0.00	1.65	1.65
	3.0	0.00	1.84	1.84
	12.0	0.00	1.96	1.96
	24.0	0.00	2.01	2.01
N,N-Dimethyl-benzamide	0.25	0.00	1.29	1.29
	0.5	0.00	1.61	1.61
	1.0	0.00	1.83	1.83
	6.0	0.00	1.94	1.94
	12.0	0.00	1.99	1.99
Capronitrile	0.25	0.00	0.48	0.48
	0.5	0.00	0.96	0.96
	3.0	0.00	1.63	1.63
	6.0	0.00	1.80	1.80
	12.0	0.00	1.95	1.95
	24.0	0.00	1.99	1.99
Benzonitrile[c]	0.25	0.00	0.65	0.65
	0.5	0.00	1.40	1.40
	1.0	0.00	1.79	1.79
	3.0	0.00	1.93	1.93
	6.0	0.00	2.00	2.00

[a,b] See corresponding footnotes in Table 1. [c] Solution changed to yellow.

substituted position of styrene oxide, the product consisting of a mixture of 26% 2- and 74% 1-phenyl-ethanol.[15] The results are summarized in Table 7.

Amides and nitriles. Primary amides liberated only 1 equiv of hydrogen slowly and the slow uptake of only 1 equiv of hydride for reduction was realized. The reduction of tertiary amides utilized 1 equiv of hydride extraordinarily rapidly, but the second equivalent was quite slow. Both capronitrile and benzonitrile utilized 2 molar equiv of hydride slowly. Somewhat unexpectedly, the reduction of benzonitrile appeared to proceed considerably more readily than the aliphatic derivative. Aluminum hydride reacted with tertiary amides and nitriles rapidly, but with primary amides slowly.[15] The results are summarized in Table 8.

Table 9. Reaction of Bis(diethylamino)aluminum Hydride with Representative Nitro Compounds an Their Derivatives in Tetrahydrofuran at 0℃

Compound[a]	Time, h	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
1-Nitropropane	0.25	0.09	0.89	0.80
	1.0	0.38	1.88	1.50
	6.0	0.64	2.53	1.89
	12.0	0.71	2.64	1.93
	24.0	0.85	2.86	2.01
Nitrobenzene	0.25	0.00	0.10	0.10
	3.0	0.00	0.89	0.89
	6.0	0.00	1.48	1.48
	12.0	0.00	1.79	1.79
	24.0	0.00	1.99	1.99
Azobenzene	6.0	0.00	0.30	0.30
	72.0	0.00	0.74	0.74
	168.0	0.00	0.75	0.75
Azoxybenzene	24.0	0.00	0.10	0.10
	168.0	0.00	0.24	0.24

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

Table 10. Reaction of Bis(diethylamino)aluminum Hydride with Representative Other Nitrogen Compounds in Tetrahydrofuran at 0℃

Compound[a]	Time, h	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Cyclohexanone oxime	0.25	0.60	1.27	0.67
	1.0	0.70	1.71	1.01
	12.0	0.96	1.97	1.01
Phenyl isocyanate	0.25	0.02	0.52	0.50
	3.0	0.04	1.04	1.00
	72.0	0.04	1.44	1.40
	168.0	0.04	1.54	1.50
Pyridine	0.25	0.02	0.69	0.67
	3.0	0.02	0.96	0.94
	12.0	0.02	1.00	0.98
	24.0	0.02	1.02	1.00
4-Picoline N-oxide[c]	0.25	0.09	1.65	1.56
	1.0	0.14	1.97	1.83
	6.0	0.25	2.19	1.94
	12.0	0.32	2.32	2.00

[a,b] See corresponding footnotes in Table 1. [c] Solution turned to be yellowish turbid.

Here also, to explore the possibility of achieving a partial reduction to the aldehydes, a limiting amount of BEAH was added to solution of primary amides, tertiary amides and nitriles at 0℃. Among them, the solution of benzamide and N,N-dimethylbenzamide afforded the corresponding aldehydes in yields of *ca.* 90%, estimated by (2,4-dinitrophenyl)hydrazine analysis.

Nitro compounds and their derivatives. Unexpectedly, nitro compounds, both aliphatic and aromatic, proved to be relatively reactive to the reagent. This is in marked

Table 11. Reaction of Bis(diethylamino)aluminum Hydride with Representative Sulfur Derivatives in Tetrahydrofuran at 0℃

Compound[a]	Time, h	Hydrogen evolved[b]	Hydride used[b]	Hydride used for reduction[b]
Di-*n*-butyl disulfide	0.5	0.13	0.17	0.04
	3.0	0.34	0.67	0.33
	24.0	0.67	1.65	0.98
	48.0	0.69	1.70	1.01
Diphenyl disulfide	0.5	0.75	1.30	0.55
	1.0	0.84	1.73	0.89
	3.0	0.98	1.98	1.00
Dimethyl sulfoxide	0.25	0.68	1.18	0.50
	1.0	0.88	1.75	0.87
	3.0	0.93	1.84	0.91
	6.0	0.99	1.97	0.98
	12.0	1.00	2.00	1.00
Diphenyl sulfone	0.25	0.00	1.08	1.08
	0.5	0.00	1.40	1.40
	1.0	0.00	1.99	1.99
	3.0	0.00	2.00	2.00
Methanesulfonic acid	0.25	0.49	0.49	0.00
	1.0	0.83	0.83	0.00
	6.0	0.98	0.98	0.00
	12.0	1.00	1.00	0.00
p-Tolunesulfonic acid monohydrate	0.25	0.95	0.95	0.00
	3.0	1.58	1.58	0.00
	6.0	1.74	1.74	0.00
	24.0	2.04	2.04	0.00
	72.0	2.29	2.29	0.00
Cyclohexyl tosylate	0.25	0.00	0.35	0.35
	1.0	0.02	0.62	0.60
	6.0	0.08	0.72	0.64
	12.0	0.08	0.84	0.76
	24.0	0.08	0.95	0.87
	72.0	0.08	1.04	0.96

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

contrast to the behavior of aluminum hydride. These compounds were relatively inert to aluminum hydride. However the reactions of azo- and azoxybenzenes appeared to be relatively inert to BEAH, similar results obtained from aluminum hydride.[15] These results are summarized in Table 9.

Other nitrogen compounds. Cyclohexanone oxime liberated 1 equiv of hydrogen slowly and utilized 1 equiv of hydride for reduction readily, corresponding to the formation of N-hydroxycyclohexylamine. Phenyl isocyanate and pyridine underwent reaction at a moderate rate, utilizing 1 equiv of hydride in 24 h. 4-Picoline N-oxide underwent relatively rapid reduction to utilize 2 equiv of hydride with slow evolution of hydrogen. Aluminum hydride reduced cyclohexanone oxime and phenyl isocyanate readily to cyclohexylamine and N-methylaniline, respectively.[15] Pyridine ring compounds were also reduced at a moderate rate. The results are summarized in Table 10.

Sulfur derivatives. Diphenyl disulfide was readily reduced in 3 h, with evolution of 1 molar equiv of hydrogen. On the other hand, di-*n*-butyl disulfide was reduced quite slowly, requiring approximately 72 h for complete reaction. Interestingly, dimethyl sulfoxide and diphenyl sulfone were readily reduced to the corresponding sulfides. Aluminum hydride reduced dimethyl sulfoxide rapidly, but the sulfone examined was inert. Methanesulfonic acid liberated slowly the theoretical quantity of hydrogen, but was not reduced. However, *p*-toluenesulfonic acid monohydrate liberated 2 equiv of hydrogen relatively fast, but the third equivalent was quite slow, being incomplete in 72 h. Cyclohexyl tosylate was slowly reduced to utilize 1 equiv of hydride in 72 h without evolution of hydrogen. The reactions of sulfonic acids with aluminimun hydride liberated the theoretical quantity of hydrogen instantly, whereas cyclohexyl tosylate exhibited only traces of reaction.[15] The results are summarized in Table 11.

Conclusion

A systematic study of the reduction of representative organic compounds with bis(diethylamino)aluminum hydride (BEAH) in THF at 0℃ has been completed. The results clearly reveal that the introduction of diethylamino group to aluminum hydride diminishes its reducing power and hence induces the reagent to be a unique reducing characteristics. However, the reducing action of BEAH is quite similar to that of aluminum hydride itself. In addition to that, the most interesting one is that the reagent shows a possibility for partial reduction of carboxylic acids, primary amides and tertiary amides to the corresponding aldehydes. An extensive examination is under way.

Experimental Section

General. All glassware used in this experiment was oven dried at 140℃ for severak hours, assembled hot, and cooled under a stream of dry nitrogen. All reactions were carried out under a static pressure of nitrogen in flasks fitted with septum-covered side arms, by using standard techniques for handling air-sensitive meterials.[16] Hypodermic syringes were used to transfer the solutions.

Materials. Tetrahydrofuran (THF) was distilled from sodium-benzophenone ketyl and stored under dry nitrogen. Sodium aluminum hydride was obtained from Ethyl Corporation and used directly. 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.

Instruments. A Hewlett-Packard 5790A FID chromatograph equipped with a Hewlett-Packard 3390A integrator/plotter, with use of 12 ft.×0.125 in. column of 10% Carbowax 20 M on 100-120 mesh Supelcoport was used for GC analysis. ^{27}Al-NMR spectra were recorded on a Bruker WP 80 SY spectrometer, and chemical shifts are with reference to Al$(H_2O)_6^{3+}$. IR spectra were taken with a Perkin-Elmer 1330 spectrophotometer equipped with a sealed liquid cell.

Preparation of sodium aluminum hydride (SAH) in THF. An oven-dried, 2-*l*, round-botton flask with a side arm equipped with a magnetic stirring bar and an adaptor was attached to a mercury bubbler. The flask was flushed with dry nitrogen and then maintained under a static pressure of nitrogen. To this flask were added *ca.* 40 g of SAH (750 mmol) and 600 m*l* of THF. The slurry was stirred for 48 h at room temperature and then allowed to stand at 0℃ to permit the undissolved materials to settle. The ^{27}Al-NMR spectrum of the resulting clear solution showed a clean quintet centered at δ 97 ppm ($J_{Al\text{-}H}=176$ Hz). The concentration of SAH in THF measured by hydrolysis was 1.2 M. This solution was used for further reactions.

Preparation of aluminum hydride in THF.[14]. By means of a double-ended needle and a mass cylinder, 500 m*l* of 1.2 M SAH 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* a reflux condenser. The solution was cooled to 0℃ and precooled 600 m*l* 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 mixture was permitted to stir for 1 h and then allowed to stand at 0℃ to permit the sodium chloride precipitate to settle. The clear supernatant solution was removed by a syringe, and diethyl ether and some THF were distilled from the solution using an aspirator. The concentration of aluminum hydride in THF was 1.80 M. The solution was used for further reactions.

Preparation of bis(diethylamino)aluminum hydride (BEAH) in THF. To 139 m*l* of 1.80 M aluminum hydride in THF (250 mmol), which was cooled to 0℃, 37.3 g of diethylamine (510 mmol) was added dropwise with vigorous stirring. The solution was then stirred for 12 h at 0℃. ^{27}Al-NMR spectrum of the resulting solution showed a broad singlet at δ 129 ppm relative to $Al(H_2O)_6^{3+}$ and IR spectrum showed a stretching absorption for Al-H around 1822 cm^{-1}. The concentration of the reagent was measured by hydrolysis to be 1.42 M. The reagent was kept under a static pressure of dry nitrogen at 0℃.

General procedure for determination of rates and stoichiometry-representative. An oven-dried, 100-m*l*, round-bottom flask fitted with rubber syringe cap on an inlet port, a magnetic stirring bar, and a bent adaptor connected to a gas buret through a reflux condenser, was immersed into an ice-water bath. To this flask were charged with 28.2 m*l* of a 1.42 M BEAH stock solution (40 mmol) and 1.8 m*l* of THF, and finally 10 m*l* of a 1 M solution of 1,2-butylene oxide in THF (10 mmol) was added with stirring at 0℃. No hydrogen was evolved. After 15 min, a 4.0-m*l* aliquot of the reaction mixture was removed and injected into a 2 N H_2SO_4-THF mixture to hydrolyze residual hydride. The hydrogen evolved amounted to 3.59 mmoles. The difference (0.41) represents the number of mmoles of hydride used per mmole of compound added. Aliquots were also removed and hydrolyzed after 0.5, 1.0, 3.0, 6.0 and 12.0 h of reaction time. At 6.0 and 12.0 h 3.01 and 3.00 mmoles of hydrogen were evolved, respectively. These values indicate that 0.99 and 1.00 equivalents of hydride at 6.0 and 12.0 h, respectively, had been utilized for reduction. Obviously the reaction was complete in 12 h (Table 7).

To determine the reaction product, 10 m*l* of the reaction mixture was removed and treated with 10% H_2SO_4 to be hydrolysed. Gas chromatographic analysis showed a mixture of 92% 2-butanol and 8% 1-butanol in a total yield of 100%, and no 1,2-butylene oxide was detected.

General procedure for stereoselectivity study. The reaction of 3,3,5-trimethyl-cyclohexanone is described as representative. To a 10 m*l* vial capped by rubber septum was added 2 m*l* of a solution of BEAH in THF (1.42 M, 2.84 mmol). The vial was kept at 0℃, and to this was added 1 m*l* of a 2 M compound in THF (2 mmol). The reaction mixture was stirred for 6 h at 0℃ and then hydrolyzed by 3 N H_2SO_4. The aqueous layer was saturated with anhydrous magnesium sulfate, and the organic layer was subjected to GC analysis to indicate the presence of 88% *trans* alcohol. The results are summarized in Table 3.

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