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Reaction of Diisobutylaluminum Hydride-Dimethyl Sulfide Complex with Selected Organic Compounds Containing Representative Functional Groups. Comparison of the Reducing Characteristics of Diisobutylaluminum Hydride and Its Dimethyl Sulfide Complex

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The approximate rate and stoichiometry of the reaction of excess diisobutylaluminum hydride-dimethyl sulfide complex (DIBAH-SMe_2) with organic compounds containing representative functional group under standardized conditions (toluene, 0 ℃) were examined in order to define the reducing characterstics of the reagent and to compare the reducing power with DIBAH itself. In general, the reducing action of the complex is similar to that of DIBAH. However, the reducing power of the complex is weaker than that of DIBAH. All of the active hydrogen compounds including alcohols, amines, and thiols evolve hydrogen slowly. Aldehydes and ketones are reduced readily and quantitatively to give the corresponding alcohols. However, DIBAH-SMe_2 reduces carboxylic acids at a faster rate than DIBAH alone to the corresponding alcohols with a partial evolution of hydrogen. Similarly, acid chlorides, esters, and epoxides are readily reduced to the corresponding alcohols, but the reduction rate is much slower than that of DIBAH alone. Both primary aliphatic and aromatic amides examined evolve 1 equiv of hydrogen rapidly and are reduced slowly to the amines. Tertiary amides readily utilize 2 equiv of hydride for reduction. Nitriles consume 1 equiv of hydride rapidly but further hydride uptake is quite slow. Nitro compounds, azobenzene, and azoxybenzene are reduced moderately. Cyclohexanone oxime liberates *ca.* 0.8 equiv of hydrogen rapidly and is reduced to the N-hydroxylamine stage. Phenyl isocyanate is rapidly reduced to the imine stage, but further hydride uptake is quite sluggish. Pyridine reacts at a moderate rate with an uptake of one hydride in 48 h, while pyridine N-oxide reacts rapidly with consumption of 2 equiv of hydride for reduction in 6h. Similarly, disulfides and sulfoxide are readily reduced, whereas sulfide, sulfone, and sulfonic acid are inert to this reagent under these reaction conditions.

Introduction

Diisobutylaluminum hydride (DIBAH) has secured its position as a common reducing agent in organic synthesis,[1] especially for conversion of ester function to aldehyde. However, most of the reduction data available are for preparative purposes; they do not show any systematic reducing characteristics toward the general organic compounds. In 1985, Yoon and Gyoung carried out a systematic study of DIBAH in toluene at 0 ℃.[2] Such an investigation has enlarged the scope of its applicability as a reducing agent.

Last year, we prepared a solution of aluminum hydride-triethylamine complex (AlH_3-NEt_3) in THF and examined its reducing characteristics systematically.[3] The aluminum hydride solution in THF is slowly destroyed at room temperature, but the complex is absolutely stable in THF at that temperature. In general, the reducing action of the complex is very similar to that observed previously for aluminum hydride itself. However, the mildness of the complex improves the selectivity of aluminum hydride itself.

It seemed of interest to investigate the reducing characteristics of DIBAH complexed with a suitable Lewis base, and compare its reducing action with DIBAH itself, in analogy to the case of aluminum hydride. DIBAH and triethylamine does not form a stable complex. Finally, we prepared a solution of diisobutylaluminum hydride-dimethyl sulfide (DIBAH-SMe_2) complex in toluene and examined the reducing charateristics of the complex toward common organic functionalities under the identical conditions, adopted previously in the study of DIBAH itself, for direct comparison.

Results and Discussion

Preparation of a Solution of Diisobutylaluminum Hydride-Dimethyl Sulfide (DIBAH-SMe_2) in Tolune. A solution of DIBAH-SMe_2 in toluene was prepared by ad-

ding 5% excess over the stoichiometric amount of dimethyl sulfide to a solution of DIBAH in toluene (Eq. 1).

$$(i\text{-Bu})_2\text{AlH} + \text{SMe}_2 \xrightarrow{\text{toluene}} (i\text{-Bu})_2\text{AlH-SMe}_2 \quad (1)$$

DIBAH-SMe₂

^{27}Al NMR of DIBAH-SMe_2 in toluene showed a broad singlet centered at δ 65 (relative to $Al(H_2O)_6^{3+}$).[4] DIBAH is very viscose liquid, but the 1 : 1 complex with dimethyl sulfide becomes non-viscose. The complex is very stable at ambient temperature; no dissociation was detected.[5] Especially noteworthy is that a solution of DIBAH-SMe_2 in toluene is quite stable toward air. Thus, no measurable hydride destruction was observed when the solution was stirred for 0.5h in contact with air.

Procedure for Rate and Stoichiometry Studies. In order to compare the reducing characteristics of these two aluminum hydrides, the identical procedure and reaction conditions with those for the study of DIBAH itself were adopted.[2] Thus, the general procedure involved preparation of a reaction mixture of DIBAH-SMe_2 (1.00 M) and the compound (0.25 M) in toluene at 0 ℃. Hydrogen evolution following addition of the compound to the reagent solution was measured. From time to time, aliquots were taken from the reaction mixture and analyzed for the remaining hydride by hydrolysis. From the difference in yields of hydrogen in the two cases, the hydride utilized by the compound for reduction was calculated. In this manner, the number of moles of hydride used by compound for hydrogen formation and the number of moles utilized for reduction were determined.

In cases where the hydride-to-compound ratio of 4 : 1 was inadequate to achive complete reduction, the hydride concentration was maintained at a constant, but the concentration of compound was reduced to give a higher ratio.

Alcohols, Phenols, Amines and Thiols (Active Hydrogen Compound). Upon reaction with DIBAH-SMe_2, all the alcohols, phenols, and thiols examined liberated hydrogen quantitatively but slowly in 6-12 h at 0 ℃. In contrast, DIBAH itself with these compounds liberated quantitatively hydrogen instantly.[2] Both the reagents reacted with *n*-hexylamine to evolve only 1 equiv of hydrogen. DIBAH required 6 h, whereas DIBAH-SMe_2 required 24 h for the liberation of hydrogen. The results are summarized in Table 1.

Aldehydes and Ketones. All of the aliphatic and aromatic aldehydes and ketones examined took up 1 equiv of hydride readily but required a little longer reaction time than the case of DIBAH itself,[2] indicating clean reductions to the corresponding alcohol. Similarly, cinnamaldehyde, an α, β-unsaturated aldehyde, utilized one hydride readily with no sign of uptake of a second hydride thereafter. This indicates clean reduction to cinnamyl alcohol, as identified in the reaction of DIBAH[2] (Eq. 2). The results are summarized in Table 1.

$$\text{Ph-CH=CH-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-H} \xrightarrow[\text{or DIBAH}]{\text{DIBAH-SMe}_2} \text{Ph-CH=CHCH}_2\text{OH} \quad (2)$$

Table 1. Reaction of Representative Organic Compounds with Excess Diisobutylaluminum Hydride and Diisobutylaluminum Hydride-Dimethyl sulfide Compex in Toluene at 0 ℃

Compound[a]	DIBAH[b]			DIBAH-SMe_2		
	Time (hr)	H_2 evoln[c]	Hydride used for redn[d]	Time (hr)	H_2 evoln[c]	Hydride used for redn[d]
			I. Active Hydrogen Compounds			
1-Hexanol	0.5	0.97	0.03	0.5	0.91	0.00
	1.0	0.97	0.03	1.0	0.95	0.00
				3.0	0.96	0.00
				6.0	1.00	0.00
Benzyl alcohol	0.5	1.01	0.00	0.5	0.83	0.00
	1.0	1.01	0.01	3.0	0.88	0.00
				6.0	0.91	0.00
				12.0	1.00	0.00
3-Hexanol	0.5	0.99	0.02	0.5	0.85	0.00
	1.0	0.99	0.02	1.0	0.92	0.00
				3.0	0.98	0.00
				6.0	1.00	0.00
3-Ethyl-3-pentanol	0.5	1.01	0.00	0.5	0.76	0.00
	1.0	1.01	0.00	3.0	0.89	0.00
				6.0	1.00	0.00
Phenol	0.5	0.98	0.03	0.5	0.87	0.00
	1.0	0.98	0.02	3.0	0.97	0.00
				6.0	1.00	0.00
n-Hexylamine	0.5	0.44	0.00	0.5	0.54	0.00
	3.0	0.87	0.00	3.0	0.67	0.00

	6.0	0.99	0.00	6.0	0.83	0.00
	12.0	1.00	0.00	12.0	0.96	0.00
				24.0	1.01	0.00
1-Hexanethiol	0.5	1.01	0.01	0.5	0.81	0.00
	1.0	1.01	0.01	3.0	0.92	0.00
				6.0	1.00	0.00
Benzenethiol	0.5	1.02	0.02	0.5	0.77	0.00
	1.0	1.02	0.01	3.0	0.93	0.00
				6.0	1.00	0.00
			II. Aldehydes and Ketones			
Caproaldehyde	0.5	0.03	1.01	0.5	0.00	0.99
	1.0	0.04	1.00	1.0	0.00	0.99
Benzaldehyde	0.5	0.01	1.00	0.5	0.00	0.93
	1.0	0.01	1.00	1.0	0.00	1.00
2-Heptanone	0.5	0.04	0.98	0.5	0.00	0.93
	1.0	0.04	0.98	1.0	0.00	0.96
				3.0	0.00	1.00
Norcamphor	0.5	0.01	0.98	0.5	0.00	0.73
	1.0	0.01	0.99	3.0	0.00	0.94
				6.0	0.00	1.01
Acetophenone	0.5	0.00	0.98	0.5	0.01	0.94
	1.0	0.00	0.98	1.0	0.01	1.00
Benzophenone	0.5	0.00	0.99	0.5	0.00	0.89
	1.0	0.00	0.99	1.0	0.00	0.96
				3.0	0.00	1.01
				3.0	0.00	1.01
Cinnamaldehyde	0.5	0.01	0.97	0.5	0.00	0.73
	1.0	0.01	0.99	1.0	0.00	0.90
	24.0	0.03	1.02	3.0	0.00	0.98
				24.0	0.00	1.01
			III. Quinonues			
p-Benzoquinone[e]	0.5	0.25	1.21	0.5	0.02	1.38
	1.0	0.29	1.24	3.0	0.04	1.81
	3.0	0.37	1.25	6.0	0.04	1.85
	6.0	0.41	1.25	12.0	0.04	2.00[f]
Anthraquinone[e]	0.5	0.04	1.46	0.5	0.48	0.47[g]
	1.0	0.08	1.79	3.0	0.54	0.69
	3.0	0.12	2.09	6.0	0.54	0.81
	6.0	0.21	2.03	24.0	0.58	1.14
				72.0	0.58	1.41
			IV. Carboxylic Acids and Acyl Derivatives			
Caproic acid	0.5	0.88	0.77	0.5	0.43	1.11
	6.0	0.88	1.21	6.0	0.43	1.49
	24.0	0.88	1.38	24.0	0.43	1.76
	48.0	0.88	1.46	48.0	0.43	1.95
				72.0	0.43	2.01
Benzoic aicd	0.5	0.43	0.70	0.5	0.53	1.05
	6.0	0.43	1.01	6.0	0.53	1.57
	24.0	0.43	1.35	24.0	0.53	1.77
	48.0	0.43	1.57	48.0	0.53	1.89
				72.0	0.53	1.99
Acetic anhydride[h]	0.5	0.00	3.55	0.5	0.00	3.67
	1.0	0.00	3.55	1.0	0.00	3.72
	3.0	0.00	3.80	3.0	0.00	3.96
	6.0	0.00	4.01	6.0	0.00	3.97
Succinic anhydride[h,i]	0.5	0.04	0.74	0.5	0.12	1.24
	1.0	0.04	1.80	1.0	0.12	1.68
	3.0	0.08	2.62	3.0	0.12	2.02

	6.0	0.12	2.96	6.0	0.13	2.74
	24.0	0.17	3.08	24.0	0.13	2.88
Phthalic anhydride[h,i]	0.5	0.04	2.22	0.5	0.15	0.87
	1.0	0.08	2.58	1.0	0.15	1.42
	3.0	0.12	2.72	3.0	0.17	1.73
	6.0	0.17	2.80	6.0	0.17	2.26
	24.0	0.29	2.86	24.0	0.17	2.83
Caproyl chloride	0.5	0.00	1.98	0.5	0.00	1.52
	1.0	0.00	2.01	1.0	0.00	1.75
				3.0	0.00	1.98
				6.0	0.00	2.01
Benzoyl chloride	0.5	0.00	1.97	0.5	0.00	1.58
	1.0	0.00	1.97	1.0	0.00	1.79
				3.0	0.00	1.92
				6.0	0.00	2.01
			V. Esters and Lactones			
Ethyl caproate	0.5	0.00	1.99	0.5	0.00	1.67
	1.0	0.00	1.99	3.0	0.00	1.87
				6.0	0.00	1.94
				12.0	0.00	2.01
Ethyl benzoate	0.5	0.02	1.99	0.5	0.00	1.37
	1.0	0.02	2.02	3.0	0.00	1.67
				6.0	0.00	1.81
				12.0	0.00	1.99
Phenyl acetate	0.5	0.00	1.99	0.5	0.00	1.51
	1.0	0.00	1.99	3.0	0.00	1.82
				6.0	0.00	1.99
γ-Butyrolactone	0.5	0.00	1.98	0.5	0.01	1.16
	1.0	0.00	1.98	3.0	0.01	1.80
				6.0	0.01	2.01
Phthalide	0.5	0.02	1.96	0.5	0.01	1.55
	1.0	0.02	1.96	3.0	0.01	1.74
				6.0	0.01	1.87
				24.0	0.01	1.93
				48.0	0.01	2.02
Isopropenyl acetate	0.5	0.01	1.97	0.5	0.00	1.65
	1.0	0.01	1.97	3.0	0.00	1.85
				6.0	0.00	1.89
				12.0	0.00	2.00
			VI. Epoxides			
1,2-Butylene oxide	0.5	0.01	0.98	0.5	0.00	0.92
	1.0	0.01	0.98	1.0	0.00	0.96
				3.0	0.00	0.97
				6.0	0.00	1.00
Cyclohexene oxide	0.5	0.00	1.00	0.5	0.00	0.85
	1.0	0.00	1.00	1.0	0.00	0.92
				3.0	0.00	1.00
Styrene oxide	0.5	0.03	1.01	0.5	0.00	0.86
	1.0	0.03	1.01	1.0	0.00	0.92
				3.0	0.00	0.96
				6.0	0.00	1.00
			VII. Amides and Nitriles			
Caproamide	0.5	0.89	0.33	0.5	0.99	0.35
	3.0	0.89	0.53	3.0	0.99	1.24
	12.0	0.89	1.28	6.0	0.99	1.45
	24.0	0.89	1.37	24.0	0.99	1.82
				48.0	0.99	2.01

Benzamide	1.0	0.96	0.03	1.0	0.99	0.56
	6.0	0.96	0.15	6.0	0.99	0.81
	12.0	0.97	0.55	24.0	0.99	0.98
	24.0	0.97	0.59	48.0	0.99	1.21
N,N-Dimethyl-	0.5	0.26	1.92	0.5	0.04	1.85
caproamide	1.0	0.26	2.03	1.0	0.04	1.92
				3.0	0.04	2.01
N,N-Dimethyl-	0.5	0.07	2.02	0.5	0.03	1.84
benzamide	1.0	0.07	2.00	1.0	0.03	1.94
				3.0	0.03	2.02
Capronitrile	0.5	0.00	1.04	0.5	0.00	0.98
	1.0	0.00	1.04	1.0	0.00	1.19
	3.0	0.00	1.08	3.0	0.00	1.20
	6.0	0.00	1.14	6.0	0.00	1.38
				48.0	0.00	1.92
				72.0	0.00	2.01
Benzonitrile	0.5	0.04	1.00	0.5	0.01	1.02
	1.0	0.04	1.00	1.0	0.01	1.09
	3.0	0.04	0.99	3.0	0.01	1.21
	6.0	0.04	1.00	24.0	0.01	1.53
			VIII. Nitro Compounds and Their Derivatives			
1-Nitropropane	1.0	0.80	1.75	1.0	0.74	1.53[a]
	6.0	0.80	1.81	6.0	0.84	1.92
	24.0	0.80	2.02	24.0	0.98	2.00
Nitrobenzene	3.0	1.08	1.62	3.0	0.82	1.72[a]
	6.0	1.08	1.78	6.0	0.88	1.80
	24.0	1.08	1.93	24.0	0.93	1.89
				48.0	0.98	1.96
Azobenzene	3.0	0.04	1.09	3.0	0.06	1.60
	6.0	0.04	1.12	6.0	0.07	1.98
	24.0	0.21	1.13	24.0	0.08	2.00
Azoxybenzene	3.0	0.73	1.18	3.0	0.79	1.19
	6.0	0.76	1.34	6.0	0.82	1.47
	9.0	0.76	2.01	24.0	0.96	1.67
	24.0	0.76	2.08	48.0	1.00	2.01
			IX. Other Nitrogen Compounds			
Cyclohexanone oxime	1.0	0.89	1.20	1.0	0.77	1.47
	6.0	0.89	1.24	6.0	0.77	1.69
	24.0	0.89	1.44	24.0	0.77	1.84
	48.0	0.89	1.58	48.0	0.77	1.93
				72.0	0.77	2.01
Phenyl isocyanate	0.5	0.01	2.31	0.5	0.00	1.95
	1.0	0.01	2.34	1.0	0.00	2.02
	6.0	0.01	2.34	6.0	0.00	2.13
	24.0	0.05	2.46	24.0	0.00	2.54
				72.0	0.00	2.79
				120.0	0.00	3.01
Pyridine	3.0	0.05	0.46	3.0	0.00	0.29
	6.0	0.05	0.88	6.0	0.00	0.63
	24.0	0.11	1.14	24.0	0.00	0.91
	48.0	0.13	1.23	48.0	0.00	1.02
Pyridine N-oxide	0.5	0.45	1.96	0.5	0.00	1.15
	1.0	0.45	1.96	1.0	0.00	1.52
				3.0	0.00	1.74
				6.0	0.00	2.01
			X. Sulfur Derivatives			
Di-*n*-butyl disulfide	0.5	1.00	0.95	0.5	0.52	0.52

	1.0	1.00	0.99	3.0	0.71	0.77
				6.0	0.79	0.84
				12.0	0.99	1.00
Diphenyl disulfide	0.5	0.51	0.50	0.5	0.61	0.63
	1.0	0.65	0.65	1.0	0.66	0.69
	6.0	0.97	1.00	3.0	0.75	0.82
				6.0	0.91	0.93
				12.0	1.01	1.01
Phenyl *n*-propyl	0.5	0.00	0.01[j]	0.5	0.00	0.00
sulfide	3.0	0.01	0.02[j]	3.0	0.00	0.00
Dimethyl sulfoxide	3.0	0.71	0.80	3.0	0.94	0.75
	6.0	0.85	0.87	6.0	1.00	0.86
	24.0	0.85	1.00	24.0	1.00	1.01
Diphenyl sulfone	0.5	0.00	0.00	0.5	0.00	0.00
	3.0	0.00	0.00	3.0	0.00	0.01
Methanesulfonic acid	0.5	0.99	0.00	0.5	0.90	0.00
	1.0	0.99	0.00	1.0	0.94	0.00
				3.0	1.00	0.00
p-Toluenesulfonic acid	0.5	2.03	0.01	0.5	2.05	0.00
monohydrate	1.0	2.03	0.01	1.0	2.05	0.00
	6.0	2.03	0.01	6.0	2.05	0.00

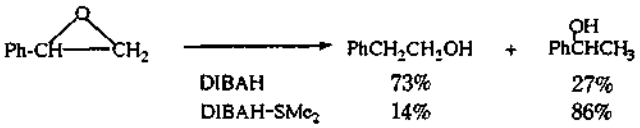
[a] Hydride to compond ratio 4 : 1, except where otherwise indicated, [b] Ref. 2, [c,d] Mol/mmol of compound, [e] Batch reaction, [f] Dark violet solution, [g] Color changed to dark green immediately, [h] Hydride to compound ratio 6 : 1, [i] Batch reaction, [j] Methyl *p*-tolyl sulfide examined.

Quinones. *p*-Benzoquinone consumed slowly 2 equiv of hydride per mole of compound for reduction without evolving any significant amount of hydrogen. These data indicate that the reaction proceeded to 1,4-dihydroxycyclohexadiene exclusively. On the other hand, anthraquinone consumed 1.41 equiv of hydride, of which *ca.* 40% was utilized for hydrogen evolution and the remaining *ca.* 60% for reduction, with an accompanying color change to dark green. This value indicates that the reaction does not involve simple reduction either to hydroquinone or to anthracenediol. In the case of DIBAH itself,[2] the reduction of *p*-benzoquinone proceeded to give a 40 : 60 distribution between hydroquinone and 1,4-dihydroxycyclohexadiene, whereas anthraquinone proceeded mainly to afford 9,10-dihydro-9,10-anthracenediol. The experimental data are summarized in Table 1.

Carboxylic Acids and Derivatives. Both caproic acid and benzoic acid evolved hydrogen only partially (0.43 and 0.53 equiv of hydrogen, respectively), suggesting that the isobutyl groups in DIBAH-SMe_2 must be reacting with active hydrogen. A similar partial hydrogen evolution was also observed in the reaction of carboxylic acids with DIBAH itself.[2] As in the case of DIBAH,[2] the reaction of DIBAH-SMe_2 with these acids consumed one hydride rapidly, with slow further reduction. Zakharkin has reported that DIBAH reduces carboxylic acids to aldehydes in 40-70% yields.[6] However, the reduction of carboxylic acids with DIBAH-SMe_2 in a limiting amount failed to stop at the aldehyde stage. Acetic anhydride consumed four hydrides in 6 h, whereas phthalic and succinic anhydride consumed about three hydrides at a moderate reduction rate with only a very slow reduction thereafter. DIBAH-SMe_2 reduced acid chlorides to the alcohol stage slowly (6 h), while DIBAH alone reduced them rapidly (0.5 h). The results are summarized in Table 1.

Esters and Lactones. DIBAH rapidly reduced esters and lactones with the uptake of 2 equiv of hydride per mol to the alcohol stage.[2] Furthermore, with 1 equiv of hydride at −78 ℃, excellent yields of aldehydes from the reduction of esters have been reported. However, the reaction of esters and lactones with DIBAH-SMe_2 requied 6 or 12 h for complete reduction and no aldehyde was formed even at −78 ℃. Isopropenyl acetate also took up 2 equiv of hydride relatively slowly. The results are summarized in Table 1.

Epoxides. All epoxides examined readily reacted with DIBAH-SMe_2, with an uptake of 1 equiv of hydride per mol of epoxide being essentially complete within 3 h. DIBAH itself reduced them rapidly within 0.5 h. Reduction of 1,2-butylene oxide with DIBAH-SMe_2 gave predominantly the S_N2-type of ring-opened products: 95% 2- and 5% 1-butanol, similar to the result with DIBAH itself. In the case of styrene oxide, however, the product distribution was dramatically reversed. Thus, DIBAH yielded 27% 1- and 73% 2-phenylethanol,[2] whereas DIBAH-SMe_2 afforded 86% 1- and 14% 2-phenylethanol. The results are summarized in Table 1.



Amides and Nitriles. Upon reaction with DIBAH-SMe_2 primary amides, similar to the case of DIBAH itself, evolved only 1 equiv of hydrogen rapidly, but the second active hydrogen was inert to this reagent. On the other hand, the reduction of primary amides with DIBAH-SMe_2 proceeded at a faster rate than the reaction with DIBAH itself to give the corresponding amines. Tertiary amides also took up 2

equiv of hydride readily in 1 h at 0 ℃. Both capronitrile and benzonitrile utilized 1 equiv of hydride rapidly, and the further reduction was much slower. The results are summarized in Table 1.

It is well known that DIBAH is a superior reagent for the synthesis of aldehydes from nitriles.[2,7] However, preliminary experiments revealed that DIBAH-SMe_2 is a much superior reagent to DIBAH itself for such conversions. Thus, DIBAH-SMe_2 in a limiting amount reduced both benzonitrile and capronitrile to the corresponding aldehydes in 90% yields. Complete results for these transformations will be reported shortly.

Nitro Compounds and Their Derivatives. 1-Nitropropane and nitrobenzene slowly consumed a total of 3 equiv of hydride, of which 2 equiv of hydride being utilized for reduction and remaining 1 equiv for hydrogen evolution, a similar pattern to the case of DIBAH itself.[2] This corresponds to the reduction to the hydroxylamine stage, as in the case of DIBAH. Unlike the case of DIBAH itself,[2] however, azobenzene utilized 2 equiv of hydride in 6 h for the reduction with evolution of a small amount of hydrogen. This suggests the fast reduction of azobenzene to aniline through the hydrazobenzene stage. Azoxybenzene uitilized 1 equiv of hydride in 1 h and the second equivalent of hydride quite slowly in 48 h with a slow evolution of hydrogen. This corresponds to the reduction to the hydrazobenzene stage. The results are summarized in Table 1.

Other Nitrogen Compounds. Like the case of DIBAH,[2] the reaction of cyclohexanone oxime with DIBAH-SMe_2 rapidly liberated 0.77 equiv of hydrogen and took up *ca.* 1 equiv of hydride for reduction with slow further reduction. This stoichiometry indicates the slow reduction to cyclohexylamine stage. Similarly, phenyl isocyanate consumed 2 equiv of hydride rapidly and the third hydride was taken up very slowly. This corresponds the slow reduction to N-methylaniline stage. Pyridine was attacked at a moderate rate and pyridine N-oxide underwent a reduction readily without evolution of hydrogen. On the other hand, the reaction of pyridine N-oxide with DIBAH itself rapidly consumed two hydrides for reduction and liberated 0.45 euqiv of hydrogen. The results are summarized in Table 1.

Sulfur Compounds. Disulfides were reduced at a moderate rate to the thiol stage, utilizing 2 mol of hydride, one hydride for reduction and the other for hydrogen evolution. DIBAH reduced di-*n*-butyl disulfide significantly faster than diphenyl disulfide, however no significant rate difference was observed in the reaction with DIBAH-SMe_2. Dimethyl sulfoxide was moderately reduced with evolution of 1 equiv of hydrogen, whereas both sulfide and sulfone examined were inert to DIBAH-SMe_2 under these reaction conditions. Methanesufonic acid evolved 1 equiv of hydrgen and *p*-toluenesulfonic acid monohydrate liberated only 2 equiv of hydrogen rapidly, similar to the case of DIBAH itself.[2] The results are summarized in Table 1.

Stereochemistry in the Reduction of Cyclic Ketones. The stereoselectivity of DIBAH-SMe_2 toward representative monocyclic and bicyclic ketones was also examined and compared with that of DIBAH itself.[2] The reduction of 2-methylcyclohexanone appeared to involve less equatorial attack but the reduction of 4-*t*-butylcyclohexanone more equatorial attack than those with DIBAH itself, yielding 23% and 65% *cis* isomers, respectively, compared to the 51% and 39% *cis* isomers with the latter reagent.[2] Reduction of bicyclic ketones, such as norcamphor and camphor, proceeded with preferential attack of DIBAH-SMe_2 from the less hindered site (93% *endo*-2-norborneol and 95% *exo*-isoborneol, respectively), similar to the results obtained by DIBAH itself. The results are summarized in Table 2.

Table 2. Stereochemistry in the Reduction of Representative Cyclic Ketones with Diisobutylaluminum Hydride-Dimethyl Sulfide Complex in Toluene at 0°[a]

Compound	Less stable isomer	Yield, %	
		DIBAH-SMe_2[b]	DIBAH[c]
2-Methylcyclohexanone	*cis*	23	51
3-Methylcyclohexanone	*trans*	44	–
4-Methylcyclohexanone	*cis*	55	–
4-*t*-Butylcyclohexanone	*cis*	65	39
3,3,5-Trimethylcyclohexanone	*trans*	90	–
Norcamphor	*endo*	90	93
Camphor	*exo*	95	84

[a]Excess reagent utilized. [b]Quantitative yields of alcohols. [c]Data taken from ref. 2.

Comparison of Reducing Characteristics of Diisobutylaluminum Hydride and Diisobutylaluminum Hydride-Dimethyl Sulfide Complex. After a safe and easy-to-handle solution of diisobutylaluminum hydride (DIBAH) became commercially available, DIBAH has turned out to be the reagent of choice for reduction and its popularity has risen considerably. Furthermore, a systematic study of DIBAH has enlarged the scope of its applicability as a reducing agent.[2] In addition, a simple addition of dimethyl sulfide to DIBAH provides a stable complex of diisobutylaluminum hydride-dimethyl sulfide (DIBAH-SMe_2). Consequently, a systematic direct comparison of reducing characteristics between DIBAH and DIBAH-SMe_2 is desirable from the standpoint of its general utility in organic synthesis and the reduction spectrum of DIBAH.

These results and the comparison study between DIBAH and DIBAH-SMe_2 are summarized in Table 1. In this table "hydrogen evolution" and "hydride used for reduction" mean the moles of hydrogen evolved and the hydride utilization only for reduction per mole of compound under investigation. In cases where no significant reduction is observed, the values listed are for the longest period for which the observation was made. Where reaction occurs, the data are for the shortest period when essentially constant values of hydrogen evolution and hydride uptake are observed. The data for DIBAH are taken from the paper published.[2]

Conclusion

This study has clearly revealed the similarities and differences in the reducing characteristics of diisobutylaluminum hydride (DIBAH) and diisobutylaluminum hydride-dimethyl sulfide (DIBAH-SMe_2) toward common organic compounds. In general, the reducing action of DIBAH-SMe_2 is similar to that observed previously for DIBAH. However, DIBAH-

SMe_2 showes a much lower reactivity than DIBAH itself. Such a relatively low reactivity could be advantageous to DIBAH in terms of the selectivity between some organic functional groups. Furthermore, DIBAH-SMe_2 shows a better partial reduction of nitriles to aldehydes than DIBAH itself. Consequently, the simple addition of dimethyl sulfide to a solution of DIBAH results in the formation of a stable complex of DIBAH-SMe_2 and, hence, broadens the reductions spectrum of DIBAH in organic synthesis.

Experimental Section

General. The reaction flasks and other glassware used in the experiments were predried at 140 ℃ for several hours, assembled hot, and cooled under a stream of nitrogen. Syringes were cooled under a stream of nitrogen and assembled. All reactions were carried out under a static pressure of nitrogen in flasks fitted with septem-covered sidearms with use of standard techniques for handling air-sensitive material.[8]

DIBAH was purchased from Aldrich Chemical Co. as a neat and diluted with freshly-distilled toluene. Most of the organic compounds utilized were commerical products of the highest purity. They were further purified by distillation or recrystallization when necessary.

Gas chromatographic analyses were carried out using a gas chromatograph equipped with 12 ft×0.125 in column of 10% Carbowax 20 M on a 100-200-mesh Supelcoport and with use of a 12 ft×0.125 in. column of 15% THEED on a 100-200-mesh Supelcoport. ^{27}Al NMR spectra were recorded on a Bruker AMX-300 spectrometer, and chemical shifts are reported relative to $Al(H_2O)_6^{3+}$.

Preparation of Diisobutylaluminum Hydride-Dimethyl Sulfide (DIBAH-SMe_2) Complex in Toluene. An oven-dried, 2-*l* flask with a sidearm equipped with a magnetic stirring bar and stopcock leading to a mercury bubbler was flushed with dry nitrogen and then maintained under a static pressure of nitrogen. To this flask was added *ca.* 140 m*l* of toluene and the flask was immersed in an ice-water bath. The DIBAH stored in cylinder was transferred to the volume of 89 m*l* (*ca.* 500 mmol) in a graduated cylinder *via* a double-ended needle, and then the DIBAH was transferred to the toluene in flask. To this was added 39 m*l* (*ca.* 550 mmol, 5% excess) of dimethyl sulfide with stirring. The resulting diisobutylaluminum hydride-dimethyl sulfide (DIBAH-SMe_2) solution in toluene at 0 ℃ was found to be 2.0 M, and the ^{27}Al NMR spectrum of the solution showed a broad singlet centered at δ 65.

The stability of DIBAH-SMe_2 and DIBAH itself toward ambient air was determined as follows. A solution of DIBAH-SMe_2 in toluene and a solution of DIBAH in toluene were placed in a beaker each. Each solution was stirred at room temperature as opened to air. From time to time, aliquots were taken from the solution and the hydride content was measured by hydrolysis with methanol. Thus, the hydride concentration of the solution of DIBAH-SMe_2 was almost constant in 0.5 h at room temperature but slowly diminished to the extent of 10% in 1 h. On the other hand, in the case of the solution of DIBAH, the hydride content was rapidly diminished to the extent of 20% in 0.5 h.

General Procedure for Determination of Rate and Stoichiometry. To a 50-m*l* flask fitted with a sidearm and capped by a rubber septum connected to a gas meter were added 10.0 m*l* of a 2.0 M solution of DIBAH-SMe_2 in toluene (20 mmol) and 5 m*l* of toluene. The flask was immersed in an ice-water bath. The reaction mixture was diluted with precooled 5.0 m*l* of toluene containing 5 mmol of the compound to be reduced. This makes the mixture 1.00 M in the reagent and 0.25 M in the compound under investigation. At different intervals, 4.0-m*l* sample aliquots were withdrawn and quenched in a methanol hydrolyzing mixture. The hydrogen evolved was measured volumetrically. The reaction was stopped when two or more analyses indicated that no more hydride was taken up. The hydrogen evolved during the reaction was measured volumetrically by an attached gas meter.

The reaction of styrene oxide is described to examplify the reduction procedure. A 50-m*l*, oven-dried, round-bottom flask, equipped with a sidearm and reflux condenser connected to a gas meter, was placed in an ice-water bath and cooled under dry nitrogen. To this flask was added 10.0 m*l* of a 2.0 M solution of DIBAH-SMe_2 (20 mmol) in toluene, followed by 5 m*l* of toluene. Five m*l* of a precooled 1.0 M solution of styrene oxide (5.0 mmol) and *n*-decane (as an internal standard) in toluene was injected into the reagent solution rapidly. Upon addition of the compound, no evolution of hydrogen was apparent. After 0.5 h, a 4.0-m*l* aliquot of the reaction mixture (1.0 mmol of the compound) was removed with a hypodermic syringe and injected into a hydrolyzing solution of methanol. The hydrogen evolved amounted to 3.15 mmol as compared to 4.01 mmol for a blank reaction (in which 5.0 m*l* of toluene was substituted for the 5.0 m*l* of the solution of the compound). This means that 0.86 mmol of hydride (0.86 mmol of the reagent) per mmol of styrene oxide had been consumed. Aliquots were also removed and hydrolyzed after 1, 3, and 6 h of the reaction time. Each produced 3.09, 3.05, and 3.01 mmol of hydrogen, indicating 1 equiv of hydride had been consumed. At the end of 6 h, the remaining mixture was hydrolyzed with methanol, followed by hydrochloric acid solution (2 M). The organic layer was separated, and analysis by GC showed 86% 1-phenylethanol and 14% 2-phenylethanol in a total yield of 99%.

General Procedure for Stereochemistry Study. The reduction of 2-methylcyclohexanone is representative. To a 10-m*l* vial capped by a rubber septum was added 2 m*l* of 2.0 M DIBAH-SMe_2 in toluene. The vial was kept at 0° with the aid of an ice-water bath. To this was added 2 m*l* of a 1.0 M solution of 2-methylcyclohexanone and *n*-dodecane (as an internal standard). The reaction mixture was stirred for 3 h at 0 ℃ and then hydrolyzed by the addition of methanol, followed by hydrochloric acid solution (2 M). The organic layer was separated and dried with anhydrous potassium carbonate. The dry organic solution was subjected to GC analysis on 10% Carbowax 20 M column, showing 23 *cis*- and 77% *trans*-2-methylcyclohexanol in a total yield of 99%.

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Reaction of Sodium Tris(diethylamino)aluminum Hydride with Selected Organic Compounds Containing Representative Functional Groups

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The approximate rates and stoichiometry of the reaction of excess sodium tris(diethylamino)aluminum hydride (STDEA) with selected organic compounds containing representative functional groups under standardized conditions (tetrahydrofuran, 0 ℃) were studied in order to characterize the reducing characteristics of the reagent for selective reductions. The reducing ability of STDEA was also compared with those of the parent sodium aluminum hydride (SAH) and lithium tris(diethylamino)aluminum hydride (LTDEA). The reagent appears to be milder than LTDEA. Nevertheless, the reducing action of STDEA is very similar to that observed previously for LTDEA, as is the case of the corresponding parent sodium and lithium aluminum hydrides. STDEA shows a unique reducing characteristics. Thus, benzyl alcohol, phenol and 1-hexanol evolved hydrogen slowly, whereas 3-hexanol and 3-ethyl-3-pentanol, secondary and tertiary alcohols, were essentially inert to STDEA. Primary amine, such as *n*-hexylamine, evolved only 1 equivalent of hydrogen slowly. On the other hand, thiols examined were absolutely stable. STDEA reduced aldehydes and ketones rapidly to the corresponding alcohols. The stereoselectivity in the reduction of cyclic ketones by STDEA was similar to that by LTDEA. Quinones, such as *p*-benzoquinone and anthraquinone, were reduced to the corresponding 1,4-dihydroxycyclohexadienes without evolution of hydrogen. Carboxylic acids and anhydrides were reduced very slowly, whereas acid chlorides were reduced to the corresponding alcohols readily. Esters and epoxides were also reduced readily. Primary carboxamides consumed hydrides for reduction slowly with concurrent hydrogen evolution, but tertiary amides were readily reduced to the corresponding tertiary amines. The rate of reduction of aromatic nitriles was much faster than that of aliphatic nitriles. Nitrogen compounds examined were also reduced slowly. Finally, disulfide, sulfoxide, sulfone, and cyclohexyl tosylate were readily reduced without evolution of hydrogen. In addition to that, the reagent appears to be an excellent partial reducing agent: llike LTDEA, STDEA converted ester and primary carboxamides to the corresponding aldehydes in good yields. Furthermore, the reagent reduced aromatic nitriles to the corresponding aldohydes chemoselectively in the presence of aliphatic nitriles. Consequently, STDEA can replace LTDEA effectively, with a higher selectivity, in most organic reductions.

Introduction

The diethylamino-derivative of lithium aluminum hydride, lithium tris(diethylamino)aluminum hydride (LTDEA), has appeared to be an attractive reducing agent[1]: it converts free carboxylic acids,[2] esters[3,4] and amides[4,5] to the corresponding aldehydes. The reagent also reduces aromatic nitriles to aldehydes chemoselectively in the presence of aliphatic nitriles intact.[4,6] Similarly, the diethylamino-derivative of sodium aluminum hydride, sodium tris(diethylamino)aluminum hydride (STDEA), has also proven to be a promising reducing agent for such transformation.[7-9] STDEA performs the conversion of carboxylic acid derivatives to aldehydes equally well. In the course of these compared experiments, we found that STDEA shows the very similar reaction trends, except for reactivity, in the reduction of organic compounds examined as LTDEA. STDEA[1] seems to be milder and, hence, more selective than LTDEA.