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Reaction of Sodium Diethyldihydroaluminate with Selected Organic Compounds Containing Representative Functional Groups†

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The approximate rates and stoichiometry of the reaction of excess sodium diethyldihydroaluminate (SDDA) with 68 selected organic compounds containing representative functional groups were examined under standard conditions (THF-toluene, 0℃) in order to compare its reducing characteristics with lithium aluminum hydride (LAH), aluminum hydride, and diisobutylaluminum hydride (DIBAH) previously examined, and enlarge the scope of its applicability as a reducing agent. Alcohols, phenol, thiols and amines evolve hydrogen rapidly and quantitatively. Aldehydes and ketones of diverse structure are reduced rapidly to the corresponding alcohols. Reduction of norcamphor gives 11% *exo*-and 89% *endo*-norborneol. Conjugated aldehydes such as cinnamaldehyde are rapidly and cleanly reduced to the corresponding allylic alcohols. *p*-Benzoquinone is mainly reduced to hydroquinone. Hexanoic acid and benzoic acid liberate hydrogen rapidly and quantitatively, however reduction proceeds very slowly. Acid chlorides and esters tested are all reduced rapidly to the corresponding alcohols. However cyclic acid anhydrides such as succinic anhydride are reduced to the lactone stage rapidly, but very slowly thereafter. Although alkyl chlorides are reduced very slowly alkyl bromides, alkyl iodides and epoxides are reduced rapidly with an uptake of 1 equiv of hydride. Styrene oxide is reduced to give 1-phenylethanol quantitatively. Primary amides are reduced very slowly; however, tertiary amides take up 1 equiv of hydride rapidly. Tertiary amides could be reduced to the corresponding aldehydes in very good yield (>90%) by reacting with equimolar SDDA at room temperature. Hexanenitrile is reduced moderately accompanying 0.6 equiv of hydrogen evolution, however the reduction of benzonitrile proceeds rapidly to the imine stage and very slowly thereafter. Benzonitrile was reduced to give 90% yield of benzaldehyde by reaction with 1.1 equiv of hydride. Nitro compounds, azobenzene and azoxybenzene are reduced moderately at 0℃, but nitrobenzene is rapidly reduced to hydrazobenzene stage at room temperature. Cyclohexanone oxime is reduced to the hydroxylamine stage in 12 h and no further reaction is apparent. Pyridine is reduced sluggishly at 0℃, but moderately at room temperature to 1,2-dihydropyridine stage in 6 h; however further reaction is very slow. Disulfides and sulfoxides are reduced rapidly, whereas sulfide, sulfone, sulfonic acid and sulfonate are inert under these reaction conditions.

Introduction

Sodium diethyldihydroaluminate[1] (SDDA) has two available hydrides for reduction in a molecule and can be regarded as an aluminum counterpart of alkylborohydrides. Therefore it was of interest to examine the reducing characteristics of this dialkyl aluminohydride and compare with those of lithium aluminum hydride[2] (LAH), aluminum hydride[3] and diisobutylaluminum hydride[4] (DIBAH), previously studied.

†Dedicated to Professor Herbert C. Brown on the occasion of his 80th birthday.

Table 1. Hydrolysis of SDDA with Various Alcohol-THF (1 : 1) Mixtures[a]

Alcohol	Time (min)	Millimoles of gas evolved at 0℃	at 25℃
n-pentanol	10	2.15	2.34
	30	2.15	2.45
	60		2.57
	90		2.76
	120		2.76
isopropanol	10	2.15	2.34
	30	2.26	2.45
	60	2.42	2.49
	90	2.42	2.64
	120		2.64
t-butanol	10	1.96	2.30
	30	2.00	2.38
	60	2.00	2.45
	90		2.49
	120		2.57
	180		2.57

[a] 1 Mmol of SDDA (measured by 1 N HCl) in THF-toluene (1 : 1) was added to 100 m*l* of alcohol-THF (1 : 1) mixtures.

On the other hand, recently we have found that sodium diethylpiperidinohydroaluminate[5] (SDPA), prepared by the reaction of SDDA with equimolar piperidine in THF-toluene, is an excellent reagent for aldehyde synthesis from the corresponding esters. Therefore we studied the reaction of SDPA systematically with representative organic compounds in order to apply it effectively to organic synthesis. SDPA exhibited many unique properties, and it has become also necessary to examine the reaction of the parent hydride, SDDA, in order to understand the reaction of SDPA. We decided to undertake a similar systematic study of SDDA in THF-toluene at 0℃ with the concentration of hydride and compound being 0.5 equiv and 0.125 equiv respectively. Although we can study the reaction in toluene conveniently (SDDA solution in toluene is available commercially), the reaction was studied in THF-toluene, in order to keep the reaction conditions similar to those of SDPA.

Results and Discussion

Selective Hydrolysis of SDDA with Various Alcohol. First, we estimated the concentration of SDDA by hydrolyzing it with 1 N HCl solution. However, the acid solution hydrolyzes both hydride and ethyl groups in SDDA at 25℃, and give a rather large amount of gas (~100 m*l*, 4 mmol) per mmol of SDDA. Therefore, we tried to develop hydrolysis system that hydrolyze only the hydride of SDDA selectively. As the result of such efforts, we found that 1 : 1 mixture of *t*-butanol-THF hydrolyze only hydride of SDDA selectively without attacking ethyl groups at 0℃. However, the 2.57 mmol of gas evolution per mmol of SDDA at 25℃ suggests that *t*-butanol attacks not only hydride but also a considerable amount of ethyl gropus in SDDA at that temperature. The results for hydrolysis of SDDA with various alcohol are summarized in Table 1.

Procedure for Rate and Stoichiometry Study. The general procedure adopted was to add 2.5 mmol of organic compounds in 5 m*l* of THF to 5 mmol of SDDA in THF-toluene (3.9 m*l* of 1.3 M toluene solution of SDDA and 11.1 m*l* THF) to give 20 m*l* of solution at 0℃. This makes the reaction mixture 0.5 M in hydride (0.25 M in SDDA) and 0.125 M in the compound under examination. The hydrogen evolved on adding the compound to the reagent was noted. The reaction mixture was maintained at 0℃ and alliquots were removed at appropriate intervals and analyzed for "residual hydride" with *t*-butanol-THF (1 : 1) at 0℃. In this way, it was possible to establish both the rate at which reduction proceeds and the stoichiometry of the reaction, *i.e.*, the number of hydrides utillized per mole of compound when the reaction comes to an effective halt. In some cases the hydride/compourd ratio of 4 : 1 was insdequate to achieve complete reduction. In such cases the hydride concentration was kept constant but the concentration of compound was reduced to give a higher ratio.

Alcohols, Phenols, Thiols and Amines. All of the alcohols, phenols, and thiols examined liberated hydrogen instantly and quantitatively. *n*-Hexylamine also liberated 2 equiv of hydrogen, however when equimolar SDDA and *n*-hexylamine were reacted, only one mole of hydrogen evolved rapidly and further hydrogen evolution was very slow evolving only 0.2 mole more in 24 h (Eq. 1).

$$CH_3(CH_2)_4CH_2NH_2 + Na^+H_2Al^-(Et)_2 \longrightarrow Na^+CH_3(CH_2)_4CH_2\underset{\displaystyle H}{\underset{|}{N}}Al^-(Et)_2 + H_2 \quad (1)$$

It is interesting to note that SDPA[6] and DIBAH[4] react with only one active hydrogen in primary amine. Diethylamine evolved hydrogen slowly in 3 h. Ethanolamine evolved only two moles of hydrogen rapidly. The results are summarized in Table 2.

Aldehydes and Ketones. All of the aldehydes and ketones examined took up 1 equiv of hydride rapidly, indicating clean reduction to the corresponding alcohol (Eq. 2). Cinnamaldehyde and methyl vinyl ketone also utilized one hydride rapidly in 30 min with no sign of uptake of second hydride even after 6 h.

$$R_2CO + Na^+H_2Al^-(Et)_2 \longrightarrow Na^+R_2C\underset{\displaystyle H}{\underset{|}{O}}Al^-(Et)_2 \xrightarrow{H_3O^+} R_2CHOH \quad (2)$$

This suggests a clean reduction to the corresponding allylic alcohols. Indeed we obtained a 100% yield of cinnamyl alcohol without contamination of hydrocinnamyl alcohol. LAH[2] and lithium trimethoxyaluminium hydride[7] are reported to take up 2 equiv of hydride and give hydrocinnamyl alcohol. The results are summarized in Table 3.

Stereochemistry of the Reduction of Monocyclic and Bicyclic Ketones with SDDA. The stereoselectivity of the reagent toward representative cyclic ketones was also studied. The reaction conditions were the same as those

Table 2. Reaction of SDDA with Representative Alcohols, Phenols, and Thiols in THF-Toluene at 0℃

Compound[a]	Time (h)	Hydrogen evolved[b]	Hydride used[c]	Hydride used for reduction[c]
1-hexanol	0.5	1.00	1.00	0.00
	1.0	1.00	1.00	0.00
benzyl alcohol	0.5	1.04	1.04	0.00
	1.0	1.04	1.04	0.00
3-hexanol	0.5	1.05	1.05	0.00
	1.0	1.05	1.05	0.00
3-ethyl-3-pentanol	0.5	1.02	1.02	0.00
	1.0	1.02	1.02	0.00
phenol	0.5	1.05	1.05	0.00
	1.0	1.05	1.05	0.00
1-hexanethiol	0.5	1.02	1.02	0.00
	1.0	1.02	1.02	0.00
benzenethiol	0.5	1.04	1.04	0.00
	1.0	1.04	1.04	0.00
hexylamine	0.5	1.98	1.98	0.00
	1.0	1.98	1.98	0.00
	3.0	1.98	1.98	0.00
hexylamine[d]	0.5	0.85	0.85	0.00
	1.0	0.98	0.98	0.00
	2.0	1.13	1.13	0.00
	12.0	1.20	1.20	0.00
diethylamine	0.5	0.65	0.65	0.00
	1.0	0.81	0.81	0.00
	3.0	0.96	0.96	0.00
	6.0	0.98	0.98	0.00
ethanolamine	0.5	0.85	0.85	0.00
	1.0	1.92	1.92	0.00
	3.0	1.92	1.92	0.00

[a] 2.5 mmol of compound was added to 5 mmol of SDDA in 20 ml of solution (0.125 M in compound and 0.25 M in SDDA). Reaction were carried out in THF-Toluene (~16 : 4) under nitrogen at 0℃. [b] Mmol of hydrogen evolved per mmol of compound. [c] Mmol of hydride used per mmol of compound. [d] 2.5 mmol of compound was added to 2.5 mmol of SDDA in 20 ml of solution.

of the rate and stoichiometry studies. In general the stereoselectivity of SDDA was very similar to that of LAH[8]. Thus the reduction of 2-methylcyclohexanone and 4-*t*-butylcyclohexanone give 74% and 91% of more stable *trans*-isomer respectively. However in rigid bicyclic ketones, such as norcamphor and *d*-camphor, reduction proceeds with preferential attack from less hindered site, giving 89% of *endo*-2-norborneol and 91% of *exo*-isoborneol respectively. The results are summarized in Table 4.

Quinones. *p*-Benzoquinone consumed 2 equiv of hydride per mol of compound, of which 1.2 equiv was utilized for the reduction and the remaining 0.8 equiv for hydrogen evolution. This corresponds to the formation of 20% 1, 4-dihydroxycyclohexadiene and 80% hydroquinone[2]. Hydroquinone was isolated in 70% yield by the reduction with LAH[9]. Anthraquinone also consumed 2 equiv of hydride rapidly and 0.35 equiv for hydrogen evolution. These data indicate the reaction proceeded to give 65% 9,10-dihydro-9,10-anthracenediol, and 35% 9,10-dihydroxyanthracene. Sometime ago, 9,10-dihydro-9,10-anthracenediol was prepared by 9-bora-

Table 3. Reaction of SDDA with Representative Aldehydes and Ketones in THF-Toluene at 0℃

Compound[a]	Time (h)	Hydrogen evolved[b]	Hydride used[c]	Hydride used for reduction[c]
hexanal	0.5	0.04	1.04	1.00
	1.0	0.04	1.04	1.00
benzaldehyde	0.5	0.05	1.04	0.99
	1.0	0.05	1.04	0.99
2-heptanone	0.5	0.08	1.06	0.98
	1.0	0.08	1.06	0.98
norcamphor	0.5	0.06	1.11	1.05
	1.0	0.06	1.11	1.05
acetophenone	0.5	0.00	1.00	1.00
	1.0	0.00	1.00	1.00
benzophenone	0.5	0.03	1.05	1.02
	1.0	0.03	1.05	1.02
cinnamaldehyde[e]	1.0	0.03	1.01	0.98
	1.0	0.03	1.01	0.98[d]
methyl vinyl ketone	0.5	0.02	1.04	1.02
	1.0	0.02	1.04	1.02

[a-c] See the corresponding footnotes in Table 2. [d] Cinnamyl alcohol was obtained quantitatively. [e] Hydrocinnamyl alcohol was obtained in a 99% yield in toluene (Ref. 1).

Table 4. Stereochemistry of Reduction of Representative Cyclic and Bicyclic Ketones with SDDA at 0℃

Ketone[a,b]	Less stable isomer	Yield (%) SDDA	Yield (%) LAH[c]
2-methylcyclohexanone	*cis*	26	24
4-*tert*-butylcyclohexanone	*cis*	9	8
norcamphor	*endo*	89	92
camphor	*exo*	91	89

[a] 2.0 mmol of ketone was added to 4.0 mmol of SDDA. [b] Reaction time was 1 h. [c] As reported in Ref. 8.

Table 5. Reaction of SDDA with Representative Quinones in THF-Toluene at 0℃

Compound[a]	Time (h)	Hydrogen evolved[b]	Hydride used[c]	Hydride used for reduction[c]
p-benzoquinone[d,e]	0.5	0.77	1.79	1.02
	1.0	0.80	2.03	1.23
	3.0	0.80	2.04	1.24
anthraquinone[e,f]	0.5	0.31	1.98	1.67
	1.0	0.35	2.04	1.69
	3.0	0.40	2.12	1.72

[a-c] See the corresponding footnotes in Table 2. [b] Batch reaction and reverse addition. [e] Black precipitate. [f] Orange color precipitate.

Table 6. Reaction of SDDA with Representative Carboxylic Acids and Acyl Derivatives in THF-Toluene at 0℃

Compound[a]	Time (h)	Hydrogen evolved[b]	Hydride used[c]	Hydride used for reduction[c]
hexanoic acid[d,e]	0.5	1.10	1.19	0.09
	1.0	1.10	1.41	0.31
	3.0	1.12	1.58	0.46
	6.0	1.04	1.87	0.83
	12.0	1.04	2.21	1.17
	24.0	1.04	2.40	1.36
benzoic acid[d,e]	0.5	1.00	1.01	0.01
	1.0	1.00	1.01	0.01
	3.0	1.00	1.23	0.23
	6.0	1.02	2.01	0.99
	12.0	1.00	2.25	1.25
	24.0	1.02	2.42	1.40
hexanoyl chloride[d]	0.5	0.07	2.07	2.00
	1.0	0.07	2.07	2.00[f]
benzoyl chloride[d]	0.5	0.00	2.02	2.02
	1.0	0.00	2.02	2.02
acetic anhydride	0.5	0.09	2.54	2.45
	1.0	0.09	2.80	2.71
	3.0	0.09	2.92	2.83
	6.0	0.09	2.92	2.83
succinic anhydride	0.5	0.08	2.48	2.40
	1.0	0.08	2.55	2.47
	3.0	0.08	2.70	2.62
	6.0	0.08	2.73	2.65
	12.0	0.08	2.73	2.65
phthalic anhydride	0.5	0.00	1.81	1.81
	1.0	0.00	2.14	2.14
	3.0	0.00	2.16	2.16
	6.0	0.00	2.46	2.46
	12.0	0.00	2.54	2.54

[a-c] See the corresponding footnotes in Table 2. [d] White precipitate. [e] Batch reaction. [f] Hexyl alcohol was obtained in a 99% yield (GC).

tabicyclononane (9-BBN) in 79% isolated yield[10]. The results are summarized in Table 5.

Carboxylic Acids and Derivatives. Hexanoic acid and benzoic acid evolved 1 equiv of hydrogen instantly accompanying white precipitate; however reduction proceeded very slowly, presumably due to the precipitate formation. The precipitate seems to be carboxylic acid salts since no precipitate is formed in the reaction of carboxylic acid with Lewis acid type hydride such as AlH_3[3] and DIBAH[4]. But, the precipitate is formed in the reaction of hexanoic acid with Lewis base type hydrides such as LAH[2]. On the other hand, acid chlorides, both hexanoyl chloride and benzoyl chloride consumed 2.0 hydride rapidly suggesting the reduction to the corresponding alcohols. Indeed we obtained 99% yield of hexyl alcohol from hexanoyl chloride (GC). The precipitate observed should be sodium chloride. Acid anhydrides take up 2 equiv of hydride rapidly (lactone stage in the case of cyclic anhydride) but very slowly thereafter (Eq. 3). This can be understood as a combination of initial fast reduction of anhydride (similar to acid chloride) and very slow reduction of acid. The results are summarized in Table 6.

$$(R\text{-}C{=}O)_2O + 2Na^+H_2Al^-(Et)_2 \xrightarrow{\text{fast}}$$

$$Na^+R\text{-}CH_2\text{-}O\text{-}\underset{\displaystyle H}{\underset{|}{Al}}^-(Et)_2 + Na^+R\text{-}COO\text{-}\underset{\displaystyle H}{\underset{|}{Al}}^-(Et)_2 \quad (3)$$

$$\downarrow \text{very slow}$$

Table 7. Reaction of SDDA with Representative Esters and Lactones in THF-Toluene at 0℃

Compound[a]	Time (h)	Hydrogen evolved[b]	Hydride used[c]	Hydride used for reduction[c]
ethyl hexanoate	0.5	0.08	1.70	1.62
	1.0	0.08	2.12	2.04
	3.0	0.08	2.12	2.04
ethyl benzoate	0.5	0.00	2.03	2.03
	1.0	0.00	2.03	2.03[d]
γ-butyrolactone	0.5	0.00	1.99	1.99
	1.0	0.00	1.99	1.99
γ-valerolactone	0.5	0.05	2.06	2.01
	1.0	0.05	2.06	2.01
phthalide	0.5	0.00	2.01	2.01
	1.0	0.00	2.01	2.01[e]
phenyl acetate	0.5	0.03	2.00	1.97
	1.0	0.03	2.00	1.97
isopropenyl acetate	0.5	0.05	2.08	2.03
	1.0	0.05	2.08	2.03
	3.0	0.05	2.08	2.03

[a-c] See the corresponding footnotes in Table 2. [d] Benzyl alcohol was obtained in a 96% yield (GC). [e] 1,2-Benzenedimethanol was obtained in a 94% isolated yield.

Esters and Lactones. All of the esters and lactones examined reacted rapidly with the uptake of 2 equiv of hydride per mol of compound. Indeed we obtained 96% yield of benzyl alcohol by GC analysis and isolated 1,2-benzenedimethanol in 94% yield. Since we obtained almost quantitative yield of benzaldehyde from ethyl benzoate by SDPA at 0℃[5], we attempted the partial reduction of ethyl benzoate and γ-valerolactone using 1.1 equiv of hydride; however we obtained only 22% of benzaldehyde (0.5 h) and 42% of γ-valerolactol (1.0 h) both at 0℃. Isopropenyl acetate also took up 2 equiv of hydride cleanly, suggesting the formation of stable aluminum enolate (Eq. 4), in contrast to LAH[2] which consumed 3 equiv of hydride. The results are summarized in Table 7.

$$CH_3\text{-}\underset{\displaystyle CH_2}{\underset{\|}{C}}\text{-}O\text{-}\underset{\displaystyle O}{\underset{\|}{C}}\text{-}CH_3 + 2Na^+H_2Al^-(Et)_2 \longrightarrow$$

$$CH_3\text{-}\underset{\displaystyle CH_2}{\underset{\|}{C}}\text{-}O\text{-}\underset{\displaystyle H}{\underset{|}{Al}}^-(Et)_2Na^+ + CH_3CH_2\text{-}O\text{-}\underset{\displaystyle H}{\underset{|}{Al}}^-(Et)_2Na^+ \quad (4)$$

Halides. Although butyl chloride was slowly reduced, benzyl chloride was rapidly reduced to toluene. And both butyl bromide and butyl iodide were reduced instantly. This is similar to LAH and contrasted to the Lewis acid type

Table 8. Reaction of SDDA with Representative Halides in THF-Toluene at 0℃

Compound[a]	Time (h)	Hydrogen evolved[b]	Hydride used[c]	Hydride used for reduction[c]
n-butyl chloride	0.5	0.03	0.03	0.00
	1.0	0.03	0.11	0.08
	3.0	0.03	0.21	0.18
	6.0	0.03	0.33	0.30
	12.0	0.03	0.46	0.43
n-butyl chloride[d,e]	0.5	0.05	0.40	0.35
	1.0	0.07	0.70	0.63
	3.0	0.07	0.90	0.83
	6.0	0.07	1.02	0.95
	12.0	0.07	1.07	1.00
benzyl chloride[e]	0.5	0.00	1.01	1.01
	1.0	0.00	1.01	1.01
n-buty bromide[e]	0.5	0.02	0.97	0.95
	1.0	0.02	1.02	1.00
	3.0	0.02	1.02	1.00
n-butyl iodide[e]	0.5	0.00	1.03	1.03
	1.0	0.00	1.03	1.03
cyclohexyl iodide	0.5	0.04	0.13	0.09
	1.0	0.04	0.23	0.19
	3.0	0.04	0.49	0.45
	6.0	0.04	0.66	0.62
	24.0	0.04	1.04	1.00
methylene chloride[e]	0.5	0.00	0.39	0.39
	1.0	0.00	0.49	0.49
	3.0	0.00	0.67	0.67
	6.0	0.00	0.73	0.73
	12.0	0.00	0.80	0.80
chlorotrimethyl silane[e]	0.5	0.00	1.00	1.00
	1.0	0.00	1.00	1.00

[a-c] See the corresponding footnotes in Table 2. [d] At room temperature. [e] White precipitate.

hydrides such as AlH_3[3] and DIBAH[4] which are inert to halides. Cyclohexyl iodide was reduced very slowly in 24 h. Methylene chloride was reduced slowly showing it is not a proper solvent for SDDA reduction. Finally chlorotrimethylsilane was transformed to trimethylsilane rapidly. The rapid reduction of butyl bromide in THF-toluene was quite contrary to the results in toluene.[1] Therefore we studied the effect of solvent briefly. We changed the ratio of THF to toluene from 16 : 4 to 10 : 10 and to 4 : 16, but the reduction were all rapid, contrary to the very slow reduction in toluene. Indeed we obtained 96% octane from octyl bromide in THF-toluene (16 : 4), but we obtained only 7% octane and 93% unreacted octyl bromide in toluene in 1 h at 0℃ (GC). This suggests that the coordination of THF to aluminum enhances the hydride donor ability of the reagent. The results are summarized in Table 8 and 9.

Epoxides. 1,2-Butylene oxide, styrene oxide and cyclohexene oxide were all reduced rapidly in 0.5 h, and 1-methyl-1,2-cyclohexene oxide was reduced a little slowly completing in 3 h. The reduction of unsymmetrical epoxides with this reagent constantly gave more hindered alcohols exclusively, resulting from the less hindered sith hydride attack. However in toluene solvent a substantial amount of less hindered alcohol (21% of 2-phenylethanol) was realized from

Table 9. Effect of Solvent on the Reduction of Alkyl Bromide with SDDA

Compound[a]	Solvent	Time (h)	Hydride used for reduction[b]
n-butyl bromide[c]	THF-toluene	0.5	0.95
	(16 : 4)	1.0	1.00
		3.0	1.00
n-butyl bromide[c]	THF-toluene	0.5	0.92
	(10 : 10)	1.0	1.02
		3.0	1.02
n-butyl bromide[c]	THF-toluene	0.5	0.93
	(4 : 16)	1.0	1.03
		3.0	1.03
n-butyl bromide	toluene	0.5	0.07
		1.0	0.13
		3.0	0.18
		6.0	0.23
n-octyl bromide[c]	THF-toluene	0.5	0.86
	(16 : :4)	1.0	0.95[d]
		3.0	1.01
		6.0	1.01
n-octyl bromide	toluene	0.5	0.03
		1.0	0.08[e]
		3.0	0.14
		6.0	0.21
		12.0	0.28

[a] See the corresponding footnotes in Table 2. [b] Mmol per mmol of compound. [c] White precipitate [d] 96% yield of octane by GC. [e] 7% yield of octane and 93% of unreacted octyl bromide were estimated by GC.

Table 10. Reaction of SDDA with Representative Epoxides in THF-Toluene at 0℃

Compound[a]	Time (h)	Hydrogen evolved[b]	Hydride used[c]	Hydride used for reduction[c]
1,2-butylene oxide	0.5	0.00	1.01	1.01
	1.0	0.00	1.03	1.03
styrene oxide	0.5	0.04	1.04	1.00
	1.0	0.04	1.08	1.04[d]
	3.0	0.04	1.08	1.04
cyclohexene oxide	0.5	0.03	1.10	1.03
	1.0	0.09	1.12	1.03
1-methyl-1,2-cyclo-	0.5	0.03	0.44	0.41
hexene oxide	1.0	0.03	0.93	0.90
	3.0	0.03	1.06	1.03
	6.0	0.03	1.06	1.03[e]

[a-c] See corresponding footnotes in Table 2. [d] 1-Phenylethanol was obtained in a 100% yield (GC), [e] 1-Methylcyclohexanol was obtained in a 98% yield (GC).

Table 11. Regioselectivity of the Reduction of Styrene Oxide with Various Metal Hydrides at 0℃ in 1 h[a]

Hydride	Yields of alcohols	1-phenyl-ethanol	2-phenyl ethanol
LAH in THF[b]	100%	96%	4%
SDDA in THF-toluene (16 : 4)	100%	100%	0%
SDDA in THF-toluene (10 : 10)	96%	100%	0%
SDDA in THF-toluene (4 : 16)	87%[c]	100%	0%
SDDA in toluene	87%	66% (65%)[d]	21% (22%)
SDDA in THF-toluene	100%	100%	0%
AlH_3 in THF[e]	100%	74%	26%
DIBAH in THF-toluene	100%	34%	66%
DIBAH in toluene[f]	100%	27%	73%

[a]See the corresponding footnotes in Table 2. [b]Ref. 2. [c]The remaining 13% was unreacted styrene oxide (GC). [d]The figures in parenthesis are the results at room temperature, reported in Ref. 1. [e]Ref. 3. [f]Ref. 4.

Table 12. Reduction of *t*-Amides with SDDA in THF-toluene at 25℃[a]

Compound	$[H^-]/[Cpd]$	Time (h)	Aldehyde	Product[b] alcohol	Amine
N,N-dimethyl hexanamide	2	0.5	90	10	0
N,N-dimethyl benzamide	2	0.5	92	5	0

[a]*t*-Amides (2 mmol) were reduced with 2 mmol of SDDA in THF-toluene at 25℃. [b]Yields were determined by GC.

the reduction of styrene oxide. We changed the solvent composition from THF-toluene (16 : 4) to (10 : 10) and to (4 : 16); however 1-phenylethanol was the only product in all cases. This suggests that in the absence of THF, SDDA molecule has some tendency to coordinate with epoxide oxygen resulting in the production of some 2-phenylethanol, similar to AlH_3[3] and DIBAH[4], Lewis acid type hydrides. The results are summarized in Table 10 and 11.

Amides and Nitriles. Primary amides evolved 2 equiv of hydrogen rapidly; however reductions proceeded slowly. Tertiary amides took up 1 equiv of hydride rapidly and the second hydride very slowly. This suggests the possibility of aldehyde synthesis. Indeed tertiary amides could be transformed to the corresponding aldehydes conveniently by reducing with equimolar SDDA at room temperature in very good yields[11] (Table 12). But, primary amides did not give aldehydes. It is interesting to note that tertiary amides are reduced rapidly to the corresponding tertiary amines by AlH_3 and DIBAH, but to the corresponding aldehydes by limited amount of LAH or SDDA, Lewis base type hydrides. Hexanenitrile was reduced moderately accompanying 0.65 equiv of hydrogen evolution, presumabley due to the acidic α-hydrogen. On the other hand, benzonitrile was reduced to the imine stage (one hydride uptake) rapidly in 0.5 h and to the amine stage slowly in 12 h. Indeed it was possible to obtain a 90% yield of benzaldehyde by reacting with 1.1 equiv of hydride. The results are summarized in Table 13.

Table 13. Reaction of SDDA with Representative Amides and Nitriles in THF-Toluene at 0℃

Compound[a]	Time (h)	Hydrogen evolved[b]	Hydride used[c]	Hydride used for reduction[c]
hexanamide[d]	0.5	2.05		
	1.0	2.06	2.54	0.48
	3.0	2.06	3.05	0.99
	6.0	2.06	3.34	1.28
	12.0	2.06	3.48	1.42
benzamide[e]	0.5	1.89		
	1.0	1.89	2.21	0.32
	3.0	1.89	2.18	0.29
	6.0	1.89	2.33	0.44
	12.0	2.07	2.98	0.91
	24.0	2.07	3.41	1.34
benzamide[f]	0.5	2.03		
	1.0	2.03	2.98	0.95
	3.0	2.03	3.78	1.75
	6.0	2.03	4.14	2.11
N,N-dimethyl-hexanamide	0.5	0.05	1.14	1.09
	1.0	0.05	1.44	1.39
	3.0	0.05	1.51	1.46
	6.0	0.05	1.64	1.59
	12.0	0.05	1.61	1.56[h]
N,N-dimethyl-benzamide	0.5	0.03	0.91	0.88
	1.0	0.03	1.11	1.08
	3.0	0.03	1.24	1.21
	6.0	0.03	1.34	1.31
	12.0	0.03	1.41	1.38[i]
hexanenitrile[g]	0.5	0.56	1.17	0.61
	1.0	0.59	1.38	0.79
	3.0	0.62	1.56	0.94
	6.0	0.65	2.04	1.39
	12.0	0.65	2.10	1.45
benzonitrile[g]	0.5	0.05	1.00	0.95
	1.0	0.05	1.22	1.17
	3.0	0.05	1.32	1.27
	6.0	0.05	1.55	1.50
	12.0	0.05	2.07	2.02
	24.0	0.05	2.07	2.02

[a-c]See corresponding footnotes in Table 2. [d]Color changed to yellow. [e]Color changed to light yellow after 50 min, then to white after 24 h. [f]1.25 mmol of compound was added to 5 mmol of SDDA in 20 ml of solution at room temperature. [g]Color changed to yellow. [h]Caproaldehyde was obtained in a 50% yield (GC) at 12 h. [i]Benzaldehyde was obtained in a 62% yield (GC) at 12 h.

Nitro Compounds and Their Derivatives. 1-Nitropropane consumed 2.57 equiv of hydride rapidly of which 1.34 was for hydrogen evolution and 1.23 was for reduction,

Table 14. Reaction of SDDA with Representative Nitro Compounds and Their Derivatives in THF-Toluene at 0℃

Compound[a]	Time (h)	Hydrogen evolved[b]	Hydride used[c]	Hydride used for reduction[c]
niropropane[d]	0.5	1.34	2.57	1.23
	1.0	1.35	2.64	1.29
	3.0	1.35	2.78	1.43
	6.0	1.35	2.90	1.55
nitropropane[d,f]	0.5	1.61	3.44	1.83
	1.0	2.01	4.07	2.06
	3.0	2.01	4.07	2.06
nitrobenzene[e]	0.5	1.47	3.37	1.90
	1.0	1.47	3.53	2.06
	3.0	1.47	3.53	2.06
nitrobenzene[e,f]	1.0	2.44	4.98	2.54
	3.0	2.44	5.03	2.59
	6.0	2.44	5.06	2.62
azobenzene[g]	0.5	0.08	0.32	0.24
	1.0	0.11	0.47	0.36
	3.0	0.17	0.72	0.55
	6.0	0.26	1.18	0.92
azobenzene[g,h]	0.5	0.14	0.81	0.67
	1.0	0.22	0.97	0.75
	3.0	0.37	1.37	1.00
	6.0	0.51	1.54	1.03
azoxybenzene[i]	0.5	0.93	2.42	1.49
	1.0	1.03	2.54	1.51
	3.0	1.09	2.60	1.51
	6.0	1.09	2.60	1.51
azoxybenzene[f,i]	0.5	1.38	3.49	2.11
	1.0	1.52	3.66	2.14
	3.0	1.77	3.76	1.99
	6.0	2.03	4.17	2.14

[a-c] See corresponding footnotes in Table 2. [d] Color changed to white immediately. [e] Color changed to dark brown immediately. [f] 1.25 mmol of compound was added to 5 mmol of SDDA in 20 ml of solution at room temperatrue. [g] Color changed to dark brawn immediately and then to dark green after 3 h. [h] At room temperature. [i] Color changed to dark green.

and further hydride uptake was very slow. This corresponds to the fast reduction to nitrosopropane and very slow reduction to hydroxylamine. But nitropropane was reduced very rapidly in 1 h to the hydroxylamine stage at room temperature. Nitrobenzene was rapidly reduced to the hydrazobenzene stage in 0.5 h at room temperature and no further reduction was apparent. Azobenzene was reduced moderately to hydrazobenzene in 3 h at room temperature. Also, azoxybenzene was reduced rapidly to hydrazobenzene in 0.5 h at room temperature similar to LAH[2]. The results are summarized in Table 14.

Other Nitrogen Compounds. Cyclohexanone oxime consumed 1 equiv of hydride in 12 h at 0℃, after 1 equiv of rapid hydrogen evolution. This corresponds to the reduction to hydroxylamine. LAH is reported to reduce this oxime further to cyclohexylamine[2,12]. Phenyl isocyanate was rapidly reduced to hydroxymethylaniline stage in 1.0 h. Pyridine

Table 15. Reaction of SDDA with Representative Nitrogen Compounds in THF-Toluene at 0℃

Compound[a]	Time (h)	Hydrogen evolved[b]	Hydride used[c]	Hydride used for reduction[c]
cyclohexanone oxime	0.5	1.05	1.55	0.50
	1.0	1.05	1.62	0.57
	3.0	1.05	1.69	0.64
	6.0	1.05	1.77	0.72
	12.0	1.05	2.10	1.05
	24.0	1.05	1.98	0.95
phenyl isocyanate	0.5	0.07	1.84	1.77
	1.0	0.07	2.00	1.93
	3.0	0.07	2.02	1.95
	6.0	0.07	2.02	1.95
pyridine	0.5	0.03	0.04	0.01
	1.0	0.03	0.09	0.06
	3.0	0.03	0.12	0.09
pyridine[d,e]	3.0	0.04	0.43	0.39
	6.0	0.04	1.08	1.04
	12.0	0.04	1.04	1.00
pyridine *N*-oxide	0.5	0.29	1.55	1.26
	1.0	0.32	1.61	1.29
	3.0	0.32	1.95	1.63
	6.0	0.32	2.36	2.04
	12.0	0.32	2.36	2.04

[a-c] See corresponding footnotes in Table 2. [d] Color changed to yellow. [e] AT room temperature.

reacts with this reagent sluggishly at 0℃; however it is moderately reduced to 1,2-dihydropyridine stage in 6 h at room temperature. Pyridine oxide was reduced to the 1,2-dilhydropyridine stage in 1 h. The results are summarized in Table 15.

Sulfur Compounds. Methyl-*p*-tolyl sulfide proved to be stable to the reagent under the standard conditions, similar to LAH. Disulfides were reduced rapidly to the corresponding thiols with the utilization of two equiv of hydride, one for reduction and the other for hydrogen evolution. Dimethyl sulfoxide evolved hydrogen moderately in 6 h; however, hydride uptake for reduction proceeded more slowly at 0℃. In the mechanism proposed for the sulfoxide reduction with dichloroborane, prior hydride uptake and the slow hydrogen evolution were explained by the prior S-O bond cleavage[13]. This mechanism may also be applied to reductions by other hydrides such as borane[14] and aluminium hydride[3]. In these cases hydrogen evolution followed immediately since these hydrides are much stronger than dichloroborane. Therefore the prior hydrogen evolution and the following slower hydride uptake at 0℃, observed with SDDA, should require another mechanism. At room temperature, reduction of dimethyl sulfoxide to sulfide proceeded rapidly, consuming 2 hydrides. Diphenyl sullfone is almost inert to this reagent; however, it was reduced slowly at room temperature. Sulfonic acids liberated hydrogen quantitatively, but no reduction was observed at the standard conditions. Finally, cyclohexyl tosylate was inert to the reagent. But, in the presence of dialkyl aluminum hydride, DIBAH, gives almost exclusively

Table 16. Reaction of SDDA with Representative Sulfur Derivatives in THF-Toluene at 0℃

Compound[a]	Time (h)	Hydrogen evolved[b]	Hydride used[c]	Hydride used for reduction[c]
methyl *p*-tolyl sulfide	0.5	0.05	0.06	0.01
	6.0	0.02	0.03	0.01
di-*n*-butyl disulfide	0.5	0.97	2.00	1.03
	1.0	0.97	2.00	1.03
diphenyl disulfide	0.5	1.03	2.02	0.99
	1.0	1.03	2.02	0.99
dimethyl sulfoxide	0.5	0.21	0.22	0.01
	1.0	0.59	0.64	0.05
	3.0	0.93	1.03	0.10
	6.0	0.95	1.43	0.48
dimethyl sulfoxide[d,e]	1.0	1.08	1.97	0.89
	3.0	1.08	2.06	0.98
	6.0	1.08	2.10	1.02
diphenyl sulfone	0.5	0.02	0.03	0.01
	1.0	0.02	0.18	0.16
	3.0	0.02	0.17	0.15
diphenyl sulfone[d,f]	12.0	0.21	0.67	0.46
	24.0	0.54	1.07	0.53
	48.0	0.81	1.66	0.85
	72.0	0.95	1.93	0.98
methanesulfonic acid	0.5	1.03	1.05	0.02
	1.0	1.03	1.05	0.02
p-toluenesulfonic	0.5	3.05	3.05	0.00
acid monohydrate	1.0	3.05	3.05	0.00
cyclohexyl tosylate	0.5	0.02	0.03	0.01
	1.0	0.02	0.03	0.01
	3.0	0.02	0.06	0.04
	6.0	0.02	0.12	0.10

[a-c] See corresponding footnotes in Table 2. [d] At room temperature. [e] Color changed to white. [f] Color changed to yellow immediately and then to red after 30 min.

cyclohexene through elimination[4]. The results are summarized in Table 16.

Conclusion

The reducing characteristics of SDDA in THF-toluene (~16 : 4) have been studied systematically with 68 selected organic compounds containing representative functional groups. In general this reagent is similar to LAH; however, SDDA seems to be a better reagent for partial reductions such as the reduction of tertiary amides and aromatic nitriles to the corresponding aldehydes, the reduction of oxime to hydroxylamine, the reduction of pyridine to 1,2-dihydropyridine, and the reduction of cinnamyl aldehyde to cinnamyl alcohol. It is also found that the reducing characteristies of SDDA changes by the presence of THF. Thus the hydride donating power of SDDA in THF-toluene is increased tremendously than in toluene, resulting the rapid reduction of alkyl bromide and only the less hindered site hydride attack of epoxides.

Experimental Section

Materials

The standard list of compounds was essentially the same as that utilized in our earlier studies[7]. SDDA solution in toluene was puchased from Aldrich.

Procedure for Hydrolysis of SDDA

Total hydrolysis of SDDA with 1 N HCl. Into a 500 m*l* flask, which was equipped with a reflux condenser connected to a gas buret, 100 m*l* of 1 N HCl introduced, and the flask was maintained at 25℃. When 1.0 m*l* (unknown concentration) solution of SDDA in THF-toluene (1 : 1) was injected into the reaction flask, 2.84 mmol of gas evolution (H_2 and C_2H_6) was completed in 5 min. Since 1 mmol of SDDA should give 2 mmol each of H_2 and C_2H_6, the concentration of SDDA is 2.84/4=0.71(M).

Selective Hydrolysis of SDDA with Various Alcohols. The hydrolysis with *t*-butanol is described as an example. The experimental set-up was the same as in the previous experiment. Into a 500 m*l* flask, 100 m*l* of *t* butanol-THF (1 : 1) mixture was introduced, and the flask was maintained at 0℃. 1.40 m*l* (1 mmol) of 0.71 M solution of SDDA (measured by 1 N HCl) in THF-toluene (1 : 1) was injected into the reaction flask at 0℃. At appropriate intervals, the gas evolution (H_2 and C_2H_6) was measured. The amounts of gas evolved after 10, 30, and 60 min of reaction time were 1.96, 2.00, and 2.00 mmol at 0℃. These indicated that 1.96, 2.00, and 2.00 mmol of hydride had reacted per mmol of SDDA. And the reaction at 25℃ was also studied using the same procedure as at 0℃. The amounts of gas evolved after 10, 30, 60, 90, 120, and 180 min of reaction time were 2.30, 2.38, 2.45, 2.49, 2.57, and 2.57 mmol at 25℃. These indicated that 2.30, 2.38, 2.45, 2.49, 2.57, and 2.57 mmol of hydride and ethyl group had reacted per mmol of SDDA.

Procedure for Rates and Stoichiometry

All the reactions were carried out under a dry nitrogen atmosphere. The reduction of styrene oxide is described as a representative. A 50 m*l* flask was oven-dried and cooled in a dry stream of nitrogen. The flask was equipped with a reflux condenser connected to a gas buret. The flask was immersed in an ice bath, and 11.1 m*l* of THF was introduced into the reaction flask, followed by 3.9 m*l* (5 mmol) of a 1.3 M solution of SDDA in toluene. Finally, 5 m*l* (2.5 mmol) of a 0.5 M solution of styrene oxide and naphthalene in THF was injected into the reaction flask. Naphthalene was added as an internal standard. Now the reaction mixture was 0.25 M in SDDA (0.5 M in hydride) and 0.125 M in styrene oxide. 0.1 mmol of hydrogen was collected in the buret and this correspond to 0.04 mmol per mmol of styrene oxide, (0.1/0.25=0.04). After 30 min, a 2 m*l* aliquot of the reaction mixture (0.25 mmol of the compound) was removed with a hypodermic syringe and injected into a hydrolyzing solution of *t*-butanol (*t*-butanol : THF=1 : 1 solution), which was precooled to 0℃ in an ice bath. The hydrogen evolved amounted to 0.76 mmol as compared to 1.02 mmol for a blank reaction. The difference of 0.26 mmol represented the number of mmol of hydride used per 0.25 mmol of compound added. That is 1.04 mmol per mmol of compound. Aliquots were also removed and hydrolyzed after 1 and 3 h of reaction time. Both produced 0.75 mmol of hydrogen, indicating 0.27 mmol of hydride used per 0.25 mmol that is 1.08 mmol

per mmol of compound. Since the total hydride used was 1.08 mmol and hydrogen evolution was 0.04 mmol both per mmol of compound, the hydride used for reduction was 1.04 mmol. At the end of 3 h, the remaining mixture was hydrolyzed with 2 N HCl. The organic layer was separated, and analysis by GC (5% Carbowax 20 M column) showed 100% 1-phenylethanol and trace of 2-phenylethanol.

Reduction of Ethyl Benzoate to Benzyl Alcohol

A 50 m*l* flask, equipped with inlet tube and connected to a mercury bubler, was under slighly positive nitrogen pressure. Into the flask, 3.9 m*l* (5 mmol) of SDDA in toluene was placed, and 11.1 m*l* of THF was introduced. The flask was maintained at 0℃ with an ice bath, and 5 m*l* (2.5 mmol) of 0.5 M ethyl benzoate in THF was added. After 1 h, the product was decomposed with 10 m*l* of 2 N HCl solution. The organic layer was separated, and analysis by GC with 5% Carbowax 20 M column, showed 96% benzyl alcohol.

Reduction of Phthalide to 1,2-Benzenedimethanol

Into a 50 m*l* flask, similarly equipped as above, 15.4 m*l* (20 mmol) of SDDA in toluene was introduced into the 100 m*l* flask. The flask was maintained at 0℃ with an ice bath, and 20 m*l* (10 mmol) of a 0.5 M phthalide solution in THF was slowly added with vigorous stirring. After 1 h, the reaction mixture was worked up with 2 N HCl with cooling, and the resulting mixture was stirred at 0℃ for 20 min. The organic layer was separated, the aqueous layer was extracted twice with 20 m*l* portions of ether, and the combined organic layer was dried over anhydrous magnesium sulfate. The solvents were evaporated on a rotary evaporator and the resulting residue was recrystallized with hexane-ether to give 1.30 g (94%) of 1,2-benzenedimethanol as a white solid, mp. 62℃ lit.[15] mp. 63-65℃). The identity of the product was further confirmed by ^{1}H-NMR (DMSO); δ 7.26-δ 7.43 (m, 4H, Ar-H) δ 5.16 (t, 2H, CH_2-OH), δ 4.59 (d, 4H, CH_2-OH).

Reduction of γ-Lactone to Lactol

Into a 50 m*l* flask, similarly equipped as above, 4.0 m*l* (2.0 mmol) of a 0.5 M γ-valerolactone solution in THF was introduced into the 50 m*l* flask. The flask was maintained at 0℃ with an ice bath, and 0.85 m*l* (1.1 mmol) of 1.3 M SDDA in toluene was added. After 1 h, the reaction mixture was decomposed with 3 m*l* of 2 N HCl solution and reacted with 2 N HCl solution of 2,4-dinitrophenylhydrazine (2.5 mmol). Yellow precipitate was formed in 30 min. The precipitate was filtered, and dried under vacuum. There was obtained 0.24 g (42%) of 2,4-DNP; mp. 125℃ lit.[16] mp. 125-127 ℃).

Synthesis of Aldehydes from *tert*-Amides

Reduction of N,N-dimethylbenzamide is representative. Into a 50 m*l* flask, similarly equipped as above, was introduced 6.9 m*l* of toluene, followed by 2.0 m*l* (2.0 mmol) of amide in THF containing mesitylene as an internal standard. The flask was maintained at 0℃ with an ice bath. Finally, 1.1 m*l* (2.2 mmol) of 2.0 M solution of SDDA in toluene was injected into the reaction flask with stirring. After 0.5 h, 10 m*l* of acetaldehyde was added to the reaction mixture to destroy the residual hydride and the mixture was stirred vigorously for 0.5 h. It was hydrolyzed with 10 m*l* of water and extracted with 10 m*l* of ethyl ether. The organic layer was separated and dehydrated with anhydrous potassium carbonate. The dried organic layer was analyzed by GC and showed 93% yield of benzaldehyde.

Synthesis of Aldehydes from Aromatic Nitriles

Reduction of benzonitrile is representative. The experimental set-up was the same as in the previous part. Into the reaction flask was introduced 6.9 m*l* of toluene, followed by 2.0 m*l* (2.0 mmol) of benzonitrile solution containing mesitylene as an internal standard. The flask was maintained at 0℃ with an ice bath. Finally, 1.1 m*l* (2.2 mmol) of 2.0 M solution of SDDA in toluene was injected in the reaction flask with stirring. After 0.5 h, the reaction mixture was hydrolyzed with 10 m*l* (10 mmol) of 1 N sulfuric acid and extracted with 10 m*l* of ethyl ether. The ether layer was dehydrated with anhydrous potassium carbonate. The dried organic layer was analyzed by GC and showed 90% yield of benzaldehyde.

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