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Aldehyde Syntheses from Carboxylic Acid Esters with Sodium Diethyldihexylaminohydroaluminate

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Sodium diethyldihydroaluminate (SDDA) is an interesting aluminohydride which reacts with equimolar secondary amines to give the corresponding amino derivatives.² Recently we have reported that sodium diethylpiperidinohydroaluminate (SDPA) is an excellent selective reducing agent for the synthesis of aldehydes from carboxylic acid esters.³ Since diisobutyl aluminum hydride (DIBAH),⁴ lithium tris(diethylamino)aluminum hydride⁵ and diamino aluminum hydride⁶ require very low temperature (-78°C)^{4,5} or longer reaction time at elevated temperature (65°C),⁶ the excellent yields

Table 1. Reduction of Ester and Carbonyl Compounds with *sec*-Amine Derivatives of SDDA at 0°C ^{a,b}

Reactants	Products	SDPyA	SDPA	SDEA	SDHA	SDBA
Ethyl benzoate	Benzaldehyde	95%	98%	95%	94%	63%
Benzaldehyde	Benzyl alcohol	48%	50%	62%	90%	90%
Acetophenone	1-Phenethyl alcohol	47%	50%	77%	90%	90%

^aReactions were run in 1.0 mmol scale (0.2 M in compound) for 1 h at 0°C in THF-toluene and 1.1 mmol of hydride was added to compound. ^bYields were determined by GLC.

of aldehydes at 0°C by SDPA would make SDPA an excellent alternative to these hydrides for the aldehyde syntheses from esters. However we have soon found some undesirable features of SDPA.⁷ Although SDPA gives almost quantitative yields of aldehydes from aromatic esters, it gives moderate to good yields of aldehydes from aliphatic esters. SDPA reduces aldehydes only partially because hydride and piperidyl group attack the carbonyl carbon competitively. The reduction of aldehydes and ketones which have α -hydrogen with SDPA accompanies hydrogen evolution (enolization). In order to improve these undesirable feature of SDPA, we explored several other amino derivatives of SDDA, and found sodium diethyldihexylaminohydroaluminate (SDHA) is a better selective reducing agent.

We examined pyrrolidine, dibenzylamine, dihexylamine and diethylamine derivatives of SDDA, in the hope to find out the steric effect of amino group on the competition of hydride and amino group. The results are summarized in Table 1. As shown in Table 1, the competition of amino group in the reduction of aldehydes and ketones was dramatically decreased with bulky dihexylamine and dibenzylamine derivatives, however sodium diethyldibenzylaminohydroaluminate (SDBA) gave only a 63% yield of benzaldehyde from ethyl benzoate compared with a 94% yield by sodium diethyldihexylaminohydroaluminate (SDHA). Enolization of acetophenone by SDHA was also only 10% in contrast to 50% by SDPA. Therefore we tested the aldehyde syntheses from the representative aromatic and aliphatic esters with SDHA. As shown in Table 2, SDHA showed equally good results from aromatic esters, however unlike SDPA, SDHA competitively reduced nitro group as easily seen by the color change.⁷ On the other hand, SDHA showed much improved yields from aliphatic esters such as ethyl caproate and phenyl caproate. Ethyl pivalate, a hindered ester, was also reduced by SDHA in an excellent yield, however ethyl cyclohexanecarboxylate and ethyl cyclohexylacetate, to our surprise, gave only moderate yields. These yields (48% and 67%) are even lower than those (59% and 78%) obtained by SDPA.³ This suggested that these cyclohexane derivatives might be reduced to aldehydes satisfactorily by even smaller amino derivatives, SDPyA. We obtained much improved yields (77% and 96%) by SDPyA. However in the case of ethyl cinnamate, neither SDHA nor SDPyA improved the poor yield obtained by SDPA.⁸ Sodium diethyldiethylaminohydroaluminate (SDEA) showed a slightly better yield (42%). In conclusion, SDHA is a good alternative of SDPA especially for the aldehyde syntheses from aliphatic esters, and SDPyA is useful for cyclohexane derivatives.

Table 2. Partial Reduction of Representative Esters to the Corresponding Aldehydes with *sec*-Amine Derivatives of SDDA at 0°C^a

Esters	[H ⁻]/[cpd]	Time (hr)	Yields ^b of aldehydes				
			SDHA	SDPyA	SDPA	SDEA	SDBA
Aromatic							
Ethyl benzoate	1.1	0.5	94	95	98	95	63
<i>t</i> -Butyl benzoate	1.5 ^c	3.0	96		98		
Phenyl benzoate	1.1	0.5	95		97		
Ethyl 2-methylbenzoate	1.1	3.0	91		96		
Methyl 2-chlorobenzoate	1.1	3.0	96	92	93	35	
Ethyl 4-nitrobenzoate	1.1	0.5	46		98		
Aliphatic							
Ethyl caproate	1.1	1.0	98 ^d	59 ^d	85 ^d	65 ^d	50 ^d
Isopropyl caproate	1.1	1.0	92 ^d		67 ^d		
Phenyl caproate	1.1	3.0	93 ^d		57 ^d		
Ethyl decanoate	1.1	1.0	93 ^d		90 ^d		
Ethyl pivalate	1.5	3.0	93	98	61	81	
Ethyl cyclohexanecarboxylate	1.5	3.0	48	77	59	41	
Ethyl cyclohexylacetate	1.5	2.0	67 ^d	96 ^d	78 ^d		
Ethyl cinnamate	1.1	1.0	25	20	25 ^e	42	

^a See the corresponding footnotes in Table 1. ^c At room temperature. ^d Acetaldehyde quenching. ^e See Ref. 8.

Experimental

Preparation of *sec*-Amine Derivatives of SDDA.

Preparation of sodium diethyldihydroaluminat (SDHA) is described as a representative. Into a 500 mL flask, which was thoroughly dried in an oven and cooled down under nitrogen, 150 mL (300 mmol) of 2 M SDDA solution in toluene and 150 mL of THF were introduced. The solution was cooled to 0°C, and then 77.4 mL (330 mmol) of distilled dihexylamine was added with vigorous stirring. Stirring was continued for additional 6 h for complete hydrogen evolution. The resulting SDHA solution was transferred into a tightly closed bottle by a double ended needle. The solution was kept in a refrigerator under slightly positive nitrogen atmosphere. The SDHA solution thus prepared was 0.88 M in hydride as standardized by hydrolyzing with *t*-butanol-THF (1:1 mixture).

Synthesis of Caproaldehyde from Ethyl Caproate with SDHA. A 50 mL flask fitted with a rubber septum on an inlet port, a magnetic stirring bar, and connected to a mercury bubbler, was immersed in an ice bath. Into the flask, was introduced 2.8 mL of THF and 1.0 mL (1.0 mmol) of ethyl caproate solution in THF containing mesitylene as an internal standard, followed by 1.25 mL (1.1 mmol) of 0.88 M solution of SDHA in THF-toluene (1:1). The solution was maintained at 0°C with stirring. After 3 h, the reaction mixture was quenched with acetaldehyde and then hydrolyzed with 5 mL of 2 N HCl, treated with NaCl, and THF layer was separated, and the water layer was extracted with ether (20 mL×3). The combined organic layer was dried over anhydrous magnesium sulfate, and analyzed by GLPC on a FFAP 50 m capillary column; which showed a 98% yield of caproaldehyde.

Synthesis of Cyclohexanecarboxaldehyde from Ethyl Cyclohexanecarboxylate with SDPyA. A 50 mL

flask similarly equipped as above, was immersed in an ice bath. Into the flask, was introduced 2.8 mL of THF and 1.0 mL (1.0 mmol) of ethyl cyclohexanecarboxylate solution in THF containing mesitylene as an internal standard, followed by 1.70 mL (1.5 mmol) of 0.88 M solution of SDPyA in THF-toluene (1:1). The solution was maintained at 0°C with stirring. After 3 h, the reaction mixture was hydrolyzed with 5 mL of 2 N HCl, treated with NaCl, and THF layer was separated, and the water layer was extracted with ether (20 mL×3). The combined organic layer was dried over anhydrous magnesium sulfate, and analyzed by GLPC on a FFAP 50 m capillary column; which showed a 77% yield of cyclohexanecarboxaldehyde.

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