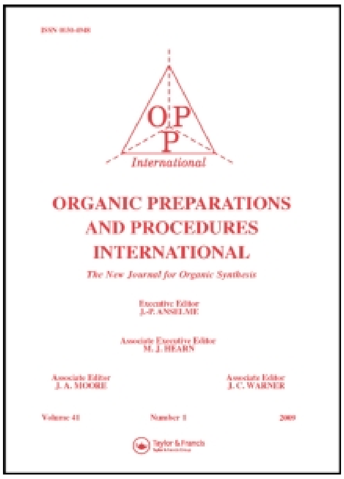

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TRANSFORMATION OF CARBOXYLIC ESTERS TO ALDEHYDES WITH SODIUM *tris*(DIETHYLAMINO)ALUMINUM HYDRIDE

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The conversion of carboxylic esters into aldehydes is important in organic synthesis. A number of useful reducing agents for such a transformation have been reported, e.g., lithium tri-*tert*-butoxyaluminum hydride,[1] diisobutylaluminum hydride,[2] sodium diisobutylaluminum hydride,[3] *bis*(4-methyl-1-piperazinyl)aluminum hydride,[4] and sodium diethylpiperidinylaluminum hydride.[5] Recently, we reported that lithium *tris*(diethylamino)aluminum hydride (LTDEA), prepared from the reaction of three equivalents of diethylamine with lithium aluminum hydride, reduces carboxylic esters to aldehydes in good yields at -78°.[6] Similarly, we synthesized the diethylamino substituted derivative of sodium aluminum hydride and applied it for conversion of carboxylic esters to aldehydes. Herein, we wish to introduce this new reducing agent, sodium *tris*(diethylamino)aluminum hydride (STDEA), which effects the transformation of esters to aldehydes in good yields at -78°.

$$\mathrm{RCO_2R'} \xrightarrow[\text{THF}]{\mathrm{Na(Et_2N)_3AlH}} \mathrm{RCHO}$$

The reagent reduces aliphatic carboxylic esters to aldehydes in yields of 60-95%. Diethyl adipate is converted to the corresponding dialdehyde with 2.2 equiv of STDEA in a yield of 64%. α,β-Unsaturated esters such as ethyl crotonate and ethyl cinnamate also undergo the reduction to afford the corresponding olefinic aldehydes in yields of 60-70%. Long chain esters (*e. g.* methyl laurate and ethyl stearate) required higher temperature to be reduced, giving the corresponding aldehydes in better than 80% yield at 0°. The reduction of aromatic esters by this reagent provides the corresponding aldehydes in 85-98% yields. The unsubstituted benzoates with a variety of alcohol portions are reduced to benzaldehyde in yields of 83-87%, showing no significant difference in the yields. Methyl-substituted benzoates such as ethyl 3- and 4-methylbenzoates afford the corresponding aldehydes in 89-92% yields. Finally, chloro and nitro groups on the benzene ring are readily accommodated and gave aldehydes in better than 94% yield.

Since STDEA[7] is milder and, hence, more selective than LTDEA,[8] this suggests that STDEA can reduce esters more selectively than LTDEA. Furthermore, the reagent can reduced esters to aldehydes readily at -78° in good yields and thus, STDEA may replace LTDEA effectively in the conversion of carboxylic esters to aldehydes.

EXPERIMENTAL SECTION

All glassware used was predried at 140° for several hours, assembled hot, dried further with a flame and cooled under a stream of dry nitrogen. All reactions and manipulations were carried out under a dry nitrogen atmosphere. All chemicals were commercial products of the highest available purity, which were further purified by standard methods before use. Tetrahydrofuran (THF) was distilled from benzophenone-sodium ketyl prior to use. Sodium aluminum hydride, received from Ethyl Corporation, was used as a clear solution in THF after removing undissolved material. Diethylamine was dried over potassium hydroxide pellet and distilled. ^{27}Al NMR spectra were recorded on a Bruker WP 80 SY spectrometer and chemical shifts are with reference to $\mathrm{Al(H_2O)_6^{3+}}$. GC analyses were performed on a Hewlett-Packard 5790A FID chromatograph equipped with a Hewlett-Packard 3390A integrator/plotter, using 12 ft. x 0.125 in. column of 10% Carbowax 20 M on 100-120 mesh Supelcoport.

Preparation of Sodium *tris*(Diethylamino)aluminum Hydride (STDEA) in THF.- To an oven-dried, 500-mL flask fitted with a side arm and a reflux condenser leading to a mercury bubbler was added 100 mL of 2 M solution of $\mathrm{NaAlH_4}$ (200 mmol) in THF and the solution was cooled to 0°. To this solution was added 46 g of diethylamine (630 mmol, 5% excess) dropwise with vigorous stirring. And than the mixture was stirred for 6 hrs at room temperature until the hydrogen evolution was complete. The resulting STDEA solution in THF was diluted with THF to be 1.0 M. The ^{27}Al NMR spectrum of the solution showed a broad singlet at δ 116 ppm.

TABLE 1. Yields of Aldehydes in the Reduction of Representative Carboxylic Esters with Sodium *tris*(Diethylamino)aluminum Hydride in Tetrahydrofuran at -78°[a]

Ester	Time (hrs)	Yield (%)[b,c]
Isopropenyl acetate	6	95
Ethyl butyrate	6	65
Ethyl isobutyrate	8	68
Ethyl isovalerate	8	62
Ethyl caproate	6	64 (62), (44)[d]
Ethyl caprylate	12	69
Methyl laurate	3	82[e]
Ethyl stearate	3	84[e]
Diethyl adipate[g]	6	64
Ethyl crotonate	6	67
Ethyl cinnamate	6	62
Methyl benzoate	24	83
Ethyl benzoate	24	86 (94), (92)[d], (90)[e], (83)[f]
Butyl benzoate	24	85
Phenyl benzoate	24	87
Ethyl 3-methylbenzoate	24	89
Ethyl 4-methylbenzoate	24	92 (96), (93)[e], (88)[f]
Methyl 3-chlorobenzoate	12	98
Methyl 4-chlorobenzoate	12	96
Ethyl 4-nitrobenzoate	24	94

a) Treated with 1.1 equiv of reagent. b) Analysis with 2,4-dinitrophenylhydrazine. The identity of the hydrazones was ascertained by their melting points. c) The figures in parenthesis are yields analyzed by GC. d) At -30°. e) At 0°. f) Treated with 2 equiv of reagent. g) Treated with 2.2 equiv of reagent.

Reduction of Carboxylic Esters.- The following procedure for the reduction of ethyl 4-methylbenzoate is illustrative. An oven-dried 50-mL flask, fitted with a side-arm and a bent adapter connected to a mercury bubbler, was charged with 10 mL of 1 M ethyl 4-methylbenzoate solution (1.64 g, 10 mmol) in THF and dodecane as an internal standard. The flask was immersed into a Dry Ice-acetone bath. To this solution was added 10 mL of 1 M STDEA solution (10 mmol) in THF dropwise with vigorous stirring and the reaction mixture was stirred for 24 hrs at -78°. An aliquot (4 mmol) of the reaction mixture was withdrawn and derivatized with 2,4-dinitrophenylhydrazine, indicating a 92% yield, mp of the hydrazone 231-233°, lit.[9] 232.5-234.5°. The rest of the reaction mixture was hydrolyzed with excess 6 M HCl and the aqueous layer was saturated with anhydrous $MgSO_4$. GC analysis of the dry THF layer indicated the presence of 4-methylbenzaldehyde in a 96% yield.[10]

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