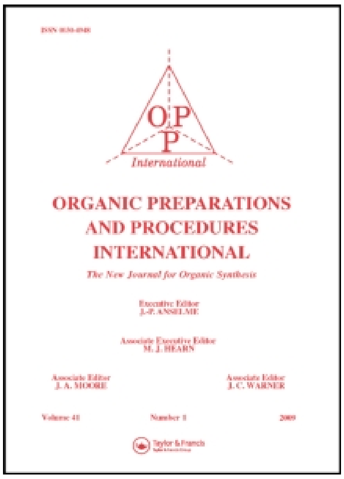

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SELECTIVE CONVERSION OF AROMATIC NITRILES TO ALDEHYDES BY LITHIUM *tris*(DIHEXYLAMINO)ALUMINUM HYDRIDE

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The conversion of nitriles into aldehydes is important in organic synthesis. Numerous useful methods have been proposed to achieve such purposes;[1] however, only one example, using potassium 9-*sec*-9-boratabicyclo[3.3.1]nonane (K 9-*sec*-Am-9-BBNH), for the chemoselective reduction of aromatic nitriles to the corresponding aldehydes has appeared in which aliphatic nitriles remain intact.[2] In the course of a systematic study of the reducing power of lithium tris(dihexylamino)aluminum hydride (LTDHA) toward selected organic compounds containing representative functional groups,[3] we found that the reagent possesses interesting reducing characteristics, indicating excellent chemoselectivity. Excess LTDHA in THF reduces aliphatic nitriles only very slowly at 0°. However, unexpectedly, reaction of aromatic nitriles with the reagent results in the immediate consumption of one equivalent of hydride for reduction and no further quantity of hydride is consumed. This remarkable feature on the rate of reaction suggested the possibility of achieving the chemoselective reduction of aromatic nitriles to aldehydes in the presence of aliphatic nitriles under practical conditions, similar to the case of selective reduction by K 9-*sec*-Am-9-BBNH.[3] This communication reports such chemoselective transformations of aromatic nitriles to the corresponding aldehydes by utilizing LTDHA which is readily prepared by treatment of $LiAlH_4$ with three equivalents of dihexylamine in THF at 0°.[4]

The reagent reduces unsubstituted aromatic nitriles, such as benzonitrile and naphthonitrile, to the corresponding aldehydes in essentially quantitative yields in 1 hr at 0° (Table 1). Dinitriles, such as phthalonitrile and terephthalonitrile, are reduced to dialdehydes in yields of 76-97%. Ring substituted derivatives are readily accommodated. Thus, chloro- and dichlorobenzo-nitriles are converted into the corresponding aldehydes in nearly quantitative yields. Tolunitriles, regardless of the position of the methyl substituent are also readily reduced to give the aldehydes in better than 98% yields. However, the yield from nitrobenzonitrile is significantly lower (62%) because of partial reduction of nitro group. Finally, cyanopyridines are also reduced to the corresponding aldehydes in essentially quantitative yields.

$$\mathrm{LiAlH_4} + 3\ \mathrm{hex_2NH} \xrightarrow[0^\circ\text{, 12 hrs}]{\text{THF}} \underset{\textbf{LTDHA}}{\mathrm{Li(hex_2N)_3AlH}} + 3\ \mathrm{H_2}\uparrow$$

TABLE 1. Yields of Aldehydes in the Reduction of Representative Aromatic Nitriles with Lithium *tris*(Dihexylamino)aluminum Hydride in Tetrahydrofuran at 0°[a]

Compound	Reaction time (hr)	Yield of aldehyde (%)[b]
benzonitrile	1	99 (96)[c](82)[d]
1-naphthonitrile	1	94
phthalonitrile	1	76
terephthalonitrile	1	97 (99)[c]
p-chlorobenzonitrile	1	98 (83)[d]
2,6-dichlorobenzonitrile	1	96
p-nitrobenzonitrile	1	62
o-tolunitrile	1	98
m-tolunitrile	1	99 (95)[c]
p-tolunitrile	1	98
3-cyanopyridine	3	98 (62)[f]
4-cyanopyridine	1	97

a) Reacted with 1 equiv of LTDHA for mononitrile and 2 equiv for dinitrile. b) Analysis with 2,4-dinitrophenylhydrazine. c) Analysis with GLPC. d) Isolated yield on distillation. e) 10% excess reagent utilized. f) Reacted for 1 h at 0°.

TABLE 2. Selective Reaction of Aromatic Nitrile in the Presence of Aliphatic Nitrile with Lithium Tris(dihexylamino)aluminum Hydride in Tetrahydrofuran at 0°[a,b]

Compound	Product	Mol %[c]
benzonitrile	benzaldehyde	92
and	benzonitrile	2
caprylonitrile	capraldehyde	0
	caprylonitrile	99
terephthalonitrile[d]	terephthaldehyde	95
and	terephthalonitrile	0
decanenitrile	decanenitrile	98

a) One equiv of the reagent per mixture of 1 equiv in each of the compounds was utilized. b) Reacted for 1 h at 0°. c) Determined by GC analysis with an internal standard and authentic samples. d) 2.0 equiv of the reagent was used.

As mentioned above, the reagent reduces aliphatic nitriles very slowly at 0°; however, aromatic nitriles are reduced to the aldehyde stages at a relatively fast rate at that temperature. Therefore, we attempted to reduce aromatic nitriles to the corresponding aldehydes chemoselectively in the presence of aliphatic nitriles intact. Indeed, as shown in Table 2, we achieved up to 92-95% conversion of aromatic nitriles into aldehydes in mixtures with aliphatic nitriles, with only minor reduction of the aliphatic nitriles, with a limiting amount of reagent.

EXPERIMENTAL SECTION

All glassware used was dried thoroughly in an oven, assembled hot, and cooled under a stream of dry nitrogen prior to use. All reactions and manipulations of air- and moisture-sensitive materials were carried out under a dry nitrogen atmosphere. All chemicals were commercial products of the highest purity, which were further purified by standard methods before use. The nitriles were commercial products and were purified either by distillation or by recrystallization. Tetrahydrofuran (THF) was distilled from benzophenone-sodium ketyl. Lithium aluminum hydride (LAH) were used directly as received from Aldrich. All of the compounds prepared have been fully characterized by ^{1}H and ^{27}Al NMR spectra. Yields reported in all cases are of analytically pure compounds unless otherwise specified. ^{1}H NMR spectra were recorded on a Varian EM-360A instrument. ^{27}Al NMR spectra were recorded on a Bruker WP 80 SY spectrometer. ^{27}Al NMR chemical shifts are with reference to $Al(H_2O)_6^{3+}$. GC analyses were carried out using a Hewlett-Packard Model 5790A FID chromatograph equipped with a Hewlett-Packard 3390A integrator/plotter.

Preparation of Lithium Tris(dihexylamino)aluminum Hydride (LTDHA) in THF.- To an oven-dried, 500-mL flask fitted with a side arm and a stopcock leading to mercury bubbler was added 100 mL of 2 M solution of LAH in THF and the solution was cooled to 0°. To this solution was added 117 g of dihexylamine (630 mmol, 5% excess) dropwise with vigorous stirring. The reaction mixture was stirred for 12 h at 0° until the evolution of hydrogen was complete. The resulting LTDHA solution in THF was diluted with THF to be 0.5 M, and the ^{27}Al NMR spectrum of the solution showed a broad singlet at δ 129.5.

Reduction of Aromatic Nitriles.- The following procedure for the reduction of benzonitrile is representative. An oven-dried 200-mL flask, equipped with a side arm, a condenser, and an adapter connected to a mercury bubbler, was flushed with nitrogen and charged with 5.47 g (53 mmol) of benzonitrile and 20 mL of THF. The solution was cooled to 0° in an ice-water bath and 106 mL of 0.5 M solution of LTDHA (53 mmol) in THF was added slowly with stirring. The reaction mixture was stirred for 1 h at 0° and analysis of an aliquot with 2,4-dinitrophenylhydrazine yielded 99% of the corresponding aldehyde. The rest of the reaction mixture (50 mmol) was further tested for isolating the aldehyde.

Isolation of Product Aldehydes.- The rest of the reaction mixture (50 mmol) was hydrolyzed with excess 3 N HCl and the mixture was then saturated with sodium chloride. The separated organic layer was treated with methanesulfonyl chloride. The supernatant solution was separated by filtration, dried with anhydrous magnesium sulfate, and subjected to fractional distillation to provide 4.35 g of benzaldehyde (82%). GC analysis showed >99% purity and ^{1}H NMR spectrum agreed with that of an authentic sample.

Competitive Reaction.- The following procedure for the competitive reaction between benzonitrile and capronitrile is representative. In the usual setup, a 50-mL flask was charged with 0.41 g of benzonitrile (4 mmol), 0.39 g of capronitrile (4 mmol), and 1.5 mL of THF. The solution was cooled to 0° in an ice-water bath and 8.0 mL of 0.5 M LTDHA (4 mmol) in THF was added rapidly with vigorous stirring. The reaction mixture was stirred for 1 h at 0° and the reaction was then quenched with water. *n*-Dodecane as an internal standard and 4 mL of ether were added and a part of organic layer was analyzed by GC for nitriles. The rest of organic layer was subjected to GC analysis for aldehydes. The combined GC analysis indicated a 92% yield of benzaldehyde and 99% of unreacted capronitrile.

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3. The reducing characteristics of LTDHA will be reported shortly.

4. The ^{27}Al NMR showed a broad singlet at δ 129.5 ppm relative to $Al(H_2O)_6^{3+}$.

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