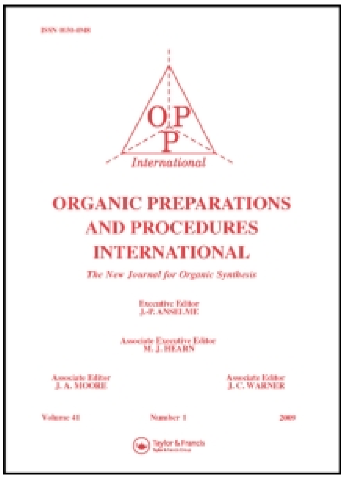

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CONVERSION OF AROMATIC NITRILES TO ALDEHYDES BY SODIUM *tris* (DIALKY-LAMINO) ALUMINUM HYDRIDES

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CONVERSION OF AROMATIC NITRILES TO ALDEHYDES BY SODIUM *tris*(DIALKYLAMINO)ALUMINUM HYDRIDES

Submitted by
(12/13/93)

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A new class of reducing agents, dialkylamino substituted derivatives of lithium aluminum hydride appears to be useful for the selective conversion of organic functionalities.[1] The chemoselective reduction of aromatic nitriles to the corresponding aldehydes in the presence of aliphatic nitriles using lithium *tris*(dihexylamino)aluminum hydride (LTDHA)[1g,2] seems to be especially promising, since this conversion is important in organic synthesis.[2-4] Very recently, we synthesized various alkoxy and dialkylamino substituted derivatives of sodium aluminum hydride and applied them in the selective reductions of organic groups. In the course of this study, we found that like LTDHA,[1g,2] the dialkylamino substituted derivatives of sodium aluminum hydride achieve the selective conversion of aromatic nitriles to aldehydes in good yields at room temperature. This communication describes such chemoselective transformations utilizing sodium *tris*(dialkylamino)aluminum hydrides.

Like lithium aluminum hydride,[1h] sodium aluminum hydride reacts readily with three equivalents of dialkylamine with the evolution three equivalents of hydrogen at 0°, even in the presence of excess amines, to form stable sodium *tris*(dialkylaminoaluminum) hydrides[5](Eq 1).

$$\mathrm{NaAlH_4} \quad + \quad 3\ \mathrm{R_2NH} \quad \xrightarrow[0^\circ \rightarrow 25^\circ]{\mathrm{THF}} \quad \mathrm{Na(R_2N)_3AlH} \quad + \quad 3\ \mathrm{H_2} \qquad (1)$$

STDEA (R = Et), STDBA (R = Bu), STDHA (R = hex)

In general, the reactivity of sodium *tris*(dialkylamino)aluminum hydrides[6] toward organic functionalities is much weaker than that of the lithium analogues,[1,7] as is the case with the parent sodium and lithium aluminum hydrides.[8,9] Nevertheless, the reducing action of the sodium derivatives is very similar to that observed previously for the lithium analogues.[8,9] A similar trend was observed in the reduction of nitriles with the sodium derivatives: although the sodium derivatives show a much lower reactivity than the lithium analogues toward nitriles, the reagent can reduce aromatic nitriles to aldehydes readily at room temperature in high yields.

As shown in Table 1, STDEA, STDBA, and STDHA are powerful enough to convert aromatic nitriles to aldehydes. STDHA, like LTDHA,[2] efficiently converts aromatic nitriles to aldehydes. The reagent reduces unsubstituted aromatic nitriles, such as benzonitrile and naphthonitrile, to the corresponding aldehydes in essentially quantitative yields in 6 hrs at 25°. Dinitriles, such as phthalonitrile and terephthalonitrile, are reduced to aldehydes in yields of 80-99%. Ring substituted derivatives are readily accommodated. Thus, chloro- and dichlorobenzonitriles are converted into the corresponding aldehydes in nearly quantitative yields. Toluonitriles, regardless of the position of the methyl substitutent, are also readily reduced to give the aldedydes in greater than 96% yields. However, the yield from *p*-nitrobenzonitrile is somewhat lower (82%) because of partial reduction of the nitro group. Finally, cyanopyridines undergo the reduction to the corresponding aldehydes equally well. All the sodium derivatives examined showed very low reactivity toward aliphatic nitriles at 25°. Reduction of aromatic nitriles to the corresponding aldehydes chemoselectively in the presence of aliphatic nitriles led to 93-99% conversion of aromatic nitriles into aldehydes in the presence of aliphatic nitriles with only minimal reduction of the aliphatic nitriles using a limiting amount of reagent.

The use of sodium aluminum hydride instead of lithium aluminum hydride for reduction of organic functionalities and preparation of other reducing agents is desirable because its lower cost and its relative mildness.[8,9] Therefore, sodium *tris*(dialkylamimo)aluminum hydrides might be reagents of choice for the chemoselective reduction of aromatic nitriles to aldehydes.

EXPERIMENTAL SECTION

All glassware 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 purchased from Aldrich

Chemical Co. and Estman Kodak Co. were purified either by distillation or by recrystallization. Tetrahydrofuran (THF) was distilled from benzophenone-sodium ketyl. Sodium aluminum hydride, received from Ethyl Corporation, was used as a clear solution in THF after removing undissolved material. 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 5790A FID chromatograph equipped with a Hewlett-Packard 3390A integrator/plotter.

TABLE 1. Yields of Aldehydes from the Reduction of Nitriles with Sodium *tris*(Dialkylamino)-aluminum Hydrides in THF[a]

Nitriles	Temp.	Yield of Aldehyde, %		
	(°C)	STDEA[b]	STDBA[b]	STDHA[c]
benzonitrile	0	81,84[g]	78[f],86,87[g]	63[f],70[g],77,88[h]
	25	90[e],97	87[f],91	70[f],85[g],97,98[h](81)[i]
1-naphthonitrile	25	94	90	96
phthalonitrile[k]	25	71	74	80
terephthalonitrile[k]	25	99	98	99
p-chlorobenzonitrile	25	98	96	97
2,6-dichlorobenzonitrile	25	91	92	96
p-nitrobenzonitrile	25	83	81	82
p-methoxybenzonitrile	25	83	93	96[j]
o-tolunitrile	25	98	94	99(82)[i]
m-tolunitrile	25	93	93	96
p-tolunitrile	25	98	97	98
3-cyanopyridine	25	31	36	93
4-cyanopyridine	25	30	37	92
hexanenitrile	0	17,18[g]	12[f],13	traces[l]
	25	19,23[g]	12[f],15	traces[l]
decanenitrile	25	16	10	traces[l]
cyclopropanecarbonitrile	25	30	22	traces[l]
isovaleronitrile	25	19	9	traces[l]

a) Reacted for 1,3 and 6 hrs in the reactions with STDEA, STDBA, and STDHA, respectively. b) Analyzed as the 2,4-dinitrophenylhydrazones. c) Analysis by GC. d) Reacted for 3 hrs. e) Reacted for 0.5 hr. f) Reacted for 1 hr. g) Reacted for 6 hrs. h) Reacted for 12 hrs. i) Isolated yield by distillation. j) Reacted for 12 hrs. k) Two equiv of the reagent was utilized. l) Unreacted starting nitriles are recovered (>95%).

Preparation of Sodium *tris*(Dialkylamino)aluminum Hydrides in THF.- The procedure for preparation of sodium *tris*(dihexylamino)aluminum hydride (STDHA) is representative. To an oven-dried, 500-mL flask fitted with a side arm and a stopcock leading to a mercury bubbler was added 100 mL of 2 M solution of $NaAlH_4$ (200 mmol) in THF; the solution was cooled to 0°. To this solution was added 117 g of dihexylamine (630 mmol, 5% excess) dropwise with vigorous stirring. The mixture was then stirred for 8 hrs at room temperature until the evolution of hydrogen was complete. The resulting STDHA solution in THF was diluted with THF to 0.5 M. The ^{27}Al NMR spectrum of the solution showed a broad singlet at δ 115.

Reduction of Aromatic Nitriles.- The following procedure for the reduction of benzonitrile with STDEA is representative. An oven-dried 50-mL flask, equipped with a side arm, a condenser, and an adapter connected to a mercury bubbler, was flushed with nitrogen and charged with 0.31 g (3 mmol) of benzonitrile and 1.5 mL of THF. The solution was maintained at 25° in a water bath and 3.3 mL of 1.0 M solution of STDEA (3.3 mmol, 10% excess) in THF was added with stirring. The reaction mixture was stirred for 1 hr at 25° and reaction with 2,4-dinitrophenylhydrazine yielded 97% of the expected 2,4-dinitrophenylhydrazone; mp 235-237° (lit.[10] mp 237°).

In the case of reduction with STDHA, the following procedure is illustrative. The reaction vessel was charged with 5.47 g (53 mmol) of benzonitrile and 20 mL of THF. The solution was maintained at 25° in a water bath and 116 mL of 0.5 M solution of STDHA (53 mmol, 10% excess) in THF was added slowly with stirring. The reaction mixture was stirred for 6 hrs at 25° and analysis of an aliquot by GC showed the presence of benzaldehyde in 98% yield. The rest of the reaction mixture (50 mmol) was used for product isolation.

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 to remove the amines which come from the reagents. The supernatant solution was separated by filtration, dried with anhydrous magnesium sulfate, and fractionally distillated to provide 4.30 g of benzaldehyde (81%): bp 177-178°, n_D^{22} 1.5452 (lit.[11] bp 178°, n_D^{20} 1.5463). GC analysis showed >99% purity and ^{1}H NMR spectrum was identified to that of an authentic sample.

Competitive Reduction.- The following procedure for the competitive reaction between benzonitrile and capronitrile with STDHA is representative. A 50-mL flask was charged with 0.41 g of benzonitrile (4 mmol), 0.39 g of hexanenitrile (4 mmol), and 1.5 mL of THF. The solution was maintained at 25° in a water bath and 8.0 mL of 0.5 M STDHA (4 mmol) in THF was added rapidly with vigorous stirring. The reaction mixture was stirred for 6 hrs at 25° 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 hydrolyzed with excess 3 N HCl and was subjected to GC analysis for aldehydes. The combined GC analysis indicated a 93% yield of benzaldehyde and 99% of unreacted hexanenitrile.

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5. The ^{27}Al NMR spectra showed a broad singlet at δ 116 for STDEA, δ 115 for STDBA, and δ 115 for STDHA, relative to $Al(H_2O)_6^{3+}$.

6. The full scope of reducing characteristics of sodium *tris*(dislkylamino)aluminum hydrides is under investigation.

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SYNTHESIS AND REACTIONS OF PHOSPHINIMINES USING HYDRAZONOYL HALIDES

Submitted by
(02/14/94)

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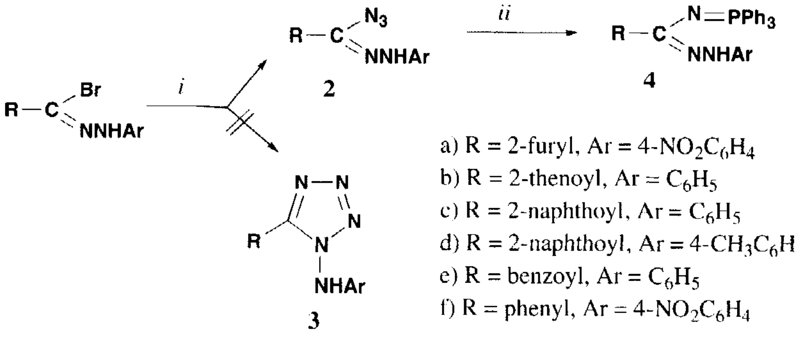
As part of our interest in the utilization of hydrazonoyl halides in heterocyclic synthesis,[1] we have investigated the preparation of azidohydrazones **2**. The azidohydrazones **2** were obtained in high yield by treatment of hydrazonoyl halides (**1**) with sodium azide under phase-transfer conditions (Eq. 1); the reaction when carried out in 80% aqueous dioxane at room temperature as previously described[2] afforded lower yields. The strong absorption band at 2120-2130 cm^{-1} in the IR spectra of the product excludes the isomeric tetrazole structure **3**. Attempts to cyclize the azidohydrazones **2** to the isomeric tetrazoles **3** by warming in inert solvents were not successful, the azidohydrazones **2** being recovered.[3] The structures of 2 were further confirmed by their conversion into the corresponding phosphonimines **4** in better than 90% yield. The IR spectra of **4** were devoid of the azide absorption band at 2120-2130 cm^{-1} region and exhibited a P=N stretching band at 1200-1300



(1)

a) R = 2-furyl, Ar = 4-$NO_2C_6H_4$
b) R = 2-thenoyl, Ar = C_6H_5
c) R = 2-naphthoyl, Ar = C_6H_5
d) R = 2-naphthoyl, Ar = 4-$CH_3C_6H_4$
e) R = benzoyl, Ar = C_6H_5
f) R = phenyl, Ar = 4-$NO_2C_6H_4$