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be proportional to the overall concentration of Ru(II) ($=$[Ru $(NH_3)_6{}^{2+}$]$+$[new species]) in the solution. It is possible, however, that the new species reacts with $O_2$ at the same rate as Ru$(NH_3)_6{}^{2+}$ does. This could give the same results as the one obtained in the present investigation. We did not attempt to rule out this possibility and the characterization of the new species was not pursured either.

In summary, the electrochemical method introduced by Anson et al.[1-3] was employed to investigate the reduction of dioxygen by hexaammineruthenium(II) at room temperature up to pH 12 from pH 1. The bimolecular rate constant measured was 70 $M^{-1}s^{-1}$ independenmt of the solution pH. The amperometric method at rotating disk electrode appears to have potential usefulness for kinetic studies of redox reactions in homogeneous solution.

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## Conversion of Aromatic Nitriles into Aldehydes by Lithium Tris(dialkylamino)aluminum Hydrides

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Easy conversion of nitrile function into aldehyde is impor-

tant in organic synthesis. Several reagents have been applied successfully for such conversion.[1] Especially noteworthy is that potassium 9-sec-amyl-9-boratabicyclo[3.3.1]nonane (K 9-sec-Am-9-BBNH) nicely achieved the chemoselective reduction of aromatic nitriles to the corresonding aldehydes in the presence of aliphatic nitriles.[2]

Recently, we synthesized various dialkylamino-substituted derivatives of lithium aluminum hydride and have been investigating the reducing properties of the derivatives.[3] In this course we found that lithium tris(dihexylamino)aluminum hydride (LTDHA) converts aromatic nitriles into aldehydes in excellent yields. Accordingly, we examined other analogous, lithium tris(diethylamino)aluminum hydride (LTDEA) and lithium tris(dibutylamino)aluminum hydride (LTDBA), in order to probe the structural features of dialkylamino-substituents in the conversion of nitrile function into aldehyde.

The dialkylamino-substituted derivatives are readily prepared by treating LiAlH$_4$ with 3 equiv of the corresponding dialkylamines in THF at 0°C (Eq 1).[4]

$$LiAlH_4 + 3R_2NH \xrightarrow[\text{0°C, <12 h}]{\text{THF}} Li(R_2N)_3AlH + 3H_2 \uparrow \qquad (1)$$
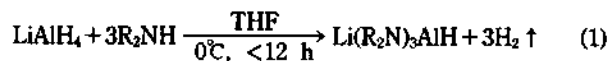
$$\begin{array}{ll} \text{LTDEA} & (R=Et) \\ \text{LTDBA} & (R=Bu) \\ \text{LTDHA} & (R=Hex) \end{array}$$

In general, as shown in Table 1, the yields of aldehydes in the reduction of aromatic nitriles are in order of LTDEA<LTDBA<LTDHA. The alkyl group evidently plays a role in obtaining high yields of aldehydes. Thus, as the length of alkyl-chain increases the yields become higher. LTDEA seems to be too reactive to stop at the aldehyde stage. LTDBA is also good enough to convert aromatic nitriles into aldehydes. However, LTDHA reduces various nitriles, except for nitrobenzonitrile, to aldehydes in essentially quantitative yields. The yield from nitrobenzonitrile is significantly low (62%), due to the reduction of nitro group itself by this reagent. Dinitriles, such as phthalonitrile and terephthalonitrile, are reduced to aldehydes in yields of 76-97%. LTDHA also converts cyanopyridines into the corresponding aldehydes in esssentially quantitative yields. As a result, this reagent appears to be superior to K 9-sec-Am-9-BBNH in the conversion of aromatic nitrile function into aldehyde stage.

The reduction of aliphatic nitriles with these reagents appears to be unsuccessful. In addition, sequence for yielding aldehydes is in the reverse order. Examination of the reaction mixture of LTDHA reveals that almost all the starting nitriles is unreacted. This remarkable feature in the rate of reaction suggests the possibility of achieving the chemoselective reduction of aromatic nitriles to aldehydes in the presence of aliphatic nitriles. In fact, LTDHA in a limiting amount reacted only with benzonitrile in the equimolar mixture of benzonitrile and hexanenitrile at 0°C to provide benzaldehyde in a yield of 93%, whereas hexanenitrile being intact.

The following procedure for the reduction of benzonitrile is described as a representative. An oven-dried 50-m*l* flask, equipped with side arm and an adaptor connected to a mercury bubbler, was flushed with anhydrous nitrogen and charged with 0.41 g (4 mmol) of benzonitrile and 2 m*l* of THF.

**Table 1.** Yields of Aldehydes in the Reduction of Nitriles with LTDEA, LTDBA, and LTDHA in Tetrahydrofuran

| Nitrile | Temp. °C | Time hr | Ratio of H⁻ to cpd | Yield of aldehyde, %[a] | | |
|---|---|---|---|---|---|---|
| | | | | LTDEA | LTDBA | LTDHA |
| benzonitrile | 0 | 1.0 | 1.0 | 60 | 69 | 99(96)[b](81)[c] |
| | | | 1.1 | 71 | 83 | 86 |
| | 25 | 0.5 | 1.0 | 93 | 98 | 99 |
| o-tolunitrile | 0 | 1.0 | 1.0 | – | – | 98 |
| | | | 1.1 | – | 83 | – |
| | 25 | 0.5 | 1.1 | 64 | – | – |
| m-tolunitrile | 0 | 1.0 | 1.0 | – | – | 99(95)[b] |
| | | | 1.1 | 70 | 83 | – |
| | 25 | 0.5 | 1.1 | 74 | – | – |
| p-methoxybenzonitrile | 0 | 1.0 | 1.0 | – | 95 | 97 |
| | 25 | 0.5 | 1.1 | 86 | – | – |
| p-chlorobenzonitrile | 0 | 1.0 | 1.0 | – | 90 | 98(83)[c] |
| | 25 | 0.5 | 1.0 | 92 | – | – |
| 2,6-dichlorobenzonitrile | 0 | 1.0 | 1.0 | 52 | 88 | 96 |
| | 25 | 0.5 | 1.0 | 60 | – | – |
| p-nitrobenzonitrile | 0 | 1.0 | 1.0 | 69 | 68 | 62 |
| phthalonitrile | 0 | 1.0 | 2.0 | 18 | 63 | 76 |
| terephthalonitrile | 0 | 1.0 | 2.0 | 90 | 98 | 97(99)[b] |
| 3-cyanopyridine | 0 | 1.0 | 1.0 | – | 30 | 62 |
| | | | 1.1 | – | 32 | 75 |
| | | 3.0 | 1.0 | 30 | 42 | 98 |
| | 25 | 0.5 | 1.0 | 36 | – | – |
| 4-cyanopyridine | 0 | 1.0 | 1.1 | 32 | 36 | 97 |
| | | 3.0 | 1.0 | 30 | 42 | 98 |
| | 25 | 0.5 | 1.0 | 36 | – | – |
| hexanenitrile | 0 | 1.0 | 1.0 | 21 | 6 | 0[d] |
| decanenitrile | 0 | 1.0 | 1.0 | 26 | 11 | 0[d] |

[a] Analysis with (2,4-dinitrophenyl)hydarzine. [b] Analysis with GLPC. [c] Isolated yield on distillation. [d] Unreacted starting materials are recovered (>90%).

The solution was immersed into a water bath at 25°C and 8 m*l* of 0.5 M solution of LTDHA (4 mmol) in THF was added slowly with stirring. The reaction mixture was stirred for 0.5 h at that temperature and analysis with (2,4-dinitrophenyl)hydrazine yielded 99% of the corresponding aldehyde. Similarly, LTDEA and LTDBA reduction showed the yields of 93 and 98%, respectively.

In a large scale reaction, 5.02 g (50 mmol) of benzonitrile in 20 m*l* of THF was reacted with 100 m*l* of 0.5 M solution of LTDHA (50 mmol) in THF for 1 h at 0°C. The reaction mixture was hydrolyzed with excess 3 N HCl and the mixture was then saturated with NaCl. The separated organic layer was treated with methanesulfonyl chloride to remove dihexylamine as sulfonamide. The supernatant solution was separated by filtration, dried with anhydrous MgSO₄, and subjected to fractional distillation to afford 4.30 g of benzaldehyde (81%).

The reducing power of LTDEA, LTDBA and LTDHA have been broadly characterized. Especially, LTDHA appears to be a mild, selective reducing agent, showing a unique reducing characteristics. Therefore, LTDHA should find wide applications in organic synthesis, especially in the selective conversion of aromatic nitrile function into the aldehyde stage

in the presence of aliphatic nitrile function as well as other organic functionalities in a complex molecule.

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4. The standard procedure for preparation of the dialkylamino-substituted derivatives of LiAlH4 is described in ref. 3 a. The $^{27}$Al-NMR spectra of LTDEA, LTDBA, and LTDHA showed a broad singlet at δ 120, 128 and 129.5 ppm, respectively, relative to Al(H2O)6$^{3+}$.

## Synthesis of Homoleptic Ionic Indium(III) Thiolates and Molecular Structure of (NMe4)[In(SC6 H3-2,6-Me2)4]

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Indium and its compounds have been widely used in various fields ranging from nuclear medicine to microelectronics.[1-6] Particularly, sulfur-containing indium complexes found their use in both extremes. Indium(III) complexes of thiocarbamate, alkylxanthate and dialkyldithiophosphate ligands have been exploited as blood cell labelling agents with reduced cell toxicity.[7] On the other hand, organoindium precursors involving sulfur have been employed in the improved preparation of thin transparent conducting indium oxide film.[8] Prompted by the foregoing significance of sulfur-containing indium complexes and the lack of X-ray crystallographically characterized homoleptic indium thiolate, the tetramethylammonium salts of [In(SR)4]$^-$ (1 : SR=SC6H5; 2 : SR=SC6H3-2,6-Me2) were prepared and structurally characterized, accounts of which are described in this report.

The methanolic solution of NaSR, generated *in situ* by the reaction of sodium metal (2 mmol) in *ca.* 20 m*l* of CH3OH

**Table 1.** Summary of Crystal Data, Intensity Collection, and Final Structure Refinement for (NMe4)[In(SC6H3-2,6-Me2)4]

| formular | C36H48InNS4 |
|---|---|
| f.w. | 737.8 |
| crystal system | monoclinic |
| space group | $P2_1/n$ |
| *a*, Å | 10.894(3) |
| *b*, Å | 19.313(3) |
| *c*, Å | 17.393(3) |
| β, deg | 91.74(2) |
| *V*, Å$^3$ | 3657.7(12) |
| Z | 4 |
| temp, ℃ | 23 |
| F(000) | 1524.0 |
| radiation source | MoK$_a$ (λ=0.71073 Å) |
| scan mode | ω/2θ |
| 2θ limit, deg | 2-50 |
| no. of collected data | 4970 |
| no. of unique data | 4785 |
| no. of obsd data (*F*>6σ(*F*)) | 4363 |
| no. of variables | 436 |
| R | 0.0376 |
| R$_w$ | 0.0410 |

followed by the addition of 2 mmol HSR (SR=SC6H5; SC6H3-2,6-Me2), was anaerobically treated with a solution of InCl3 (0.5 mmol) in CH3OH. The reaction mixture was stirred for 3 hrs at ambient temperature and then was treated with a solution of NMe4Br (0.5 mmol) in CH3OH, resulting in the precipitation of white microcrystalline solids which were collected and washed firstly with CH3OH and with Et2O several times. Recrystallization of the dried solid product from DMF/Et2O afforded analytically pure white crystalline (NMe4)·**1** and (NMe4)·**2** in the yield of 51 and 60%, respectively.[9] Analytical and spectroscopic data suggest 1 : 1 : 4 ratio of (NMe4)$^+$ : In(III) : (SR)$^-$ and single crystal X-ray diffraction study reveals the composition of (NMe4)[In(SC6H3-2,6-Me2)4].[10,11] In Table 1 and 2, crystallographic data and the atomic coordinates of non-hydrogen atoms for (NMe4)·**2** are listed, respectively.

The crystal structure of (NMe4)·**2** consists of well-separated cations and anions. The structure of NMe4$^+$ is not unusual and will not be discussed any further. As the ORTEP view in Figure 1 and the molecular model indicate, the geometry of the entire anion **2** lacks in symmetry, leading to $C_1$ point group symmetry. The $C_1$ nature of **2** is rather unusual since $S_4$ symmetry is common for many R4M type compounds.[13] In fact, the [M(SR)4] units in (PPh4)2[Fe(SPh)4],[14] (NEt4)[Fe(SPh)4],[15] and (NEt4)[Fe(SC6H-2,3,5,6-Me4)4][16] are known to have $S_4$ point group symmetry although the same unit in (NEt4)[Ga(SPh4)][17] has a pseudo $C_2$ axis. Four SC6H3-2,6-Me2 groups in **2** are arranged such that only two groups are related by two-fold axis while the others are not. For example, for a given pseudo $C_2$ axis defined by S1InS2 and S3InS4 planes, the S1-aryl and the S2-aryl groups are only symmetrically related. Similarly, only the S1-aryl and the S3-aryl groups are symmetric with respect to a $C_2$ axis that bisects the S1-In-S2 and the S1-In-S3 angles. Taken alone,