

LITHIUM TRIETHOXYALUMINOHYDRIDE AS A CONVENIENT REAGENT FOR
THE CONVERSION OF NITRILES TO ALDEHYDES

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The conversion of nitriles to aldehydes is a synthetic route of considerable importance.¹ Both the Stephen procedure and the partial reduction with lithium aluminum hydride are usually satisfactory for the conversion of aromatic nitriles, but are less than satisfactory for aliphatic nitriles.^{1,2,3} Our recent success in utilizing alkoxy substituted lithium aluminohydrides for the conversion of acid chlorides⁴ and of N,N-dimethylamides⁵ to aldehydes encouraged us to examine the utility of these reagents for the reduction of nitriles to aldehydes.

Lithium triethoxyaluminumhydride is conveniently synthesized in situ by adding either 3.00 moles of ethanol or 1.50 moles of ethyl acetate to one mole of lithium aluminum hydride in ether solution (1.3 M) at 0°. To this solution, maintained at 0°, one mole of the nitrile is added. After one hour at 0°, one-half volume of methanol is added to destroy residual unreacted hydride and give a homogeneous solution. The aldehyde yield is based on an analysis of an aliquot of the solution with 2,4-dinitrophenylhydrazine. The results are summarized in Table 1.

From these results, it appears that aliphatic nitriles can be converted to aldehydes by this procedure in yields of 70-80%, and aromatic nitriles, in yields of 80-90%. Consequently, the reduction of nitriles by lithium triethoxyaluminumhydride promises to provide a synthetic route from nitrile to aldehyde of some generality. We are continuing to explore the full scope of this reduction.

¹E. Mosettig, Organic Reactions Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 218-257.

²C. J. Claus and J. L. Morgenthau, Jr., J. Amer. Chem. Soc. **73**, 5005 (1951).

³S. Pietra and C. Trinchera, Gazz. chim. ital. **85**, 1705 (1955).

⁴H. C. Brown and R. F. McFarlin, J. Amer. Chem. Soc. **80**, 5372 (1958); H. C. Brown and B. C. Subba Rao, ibid. **80**, 5377 (1958).

⁵H. C. Brown and A. Tsukamoto, ibid. **81**, 502 (1959).

TABLE 1. YIELD OF ALDEHYDES IN THE REDUCTION OF NITRILES BY LITHIUM TRIETHOXYALUMINOHYDRIDE

Nitrile	Aldehyde yield, %
<u>n</u> -Butyronitrile	68
<u>n</u> -Capronitrile	69
Isobutyronitrile	81
Cyclopropanecarbonitrile	69
Cyclohexanecarbonitrile	76
Benzonitrile	96
<u>o</u> -Tolunitrile	87
α -Naphthonitrile	80
<u>o</u> -Chlorobenzonitrile	87
<u>p</u> -Chlorobenzonitrile	92
Cinnamonitrile	61

Recently, it was reported that sodium triethoxyaluminumhydride, prepared from the reaction of sodium hydride with aluminum ethoxide, successfully reduced aromatic nitriles to aldehydes, but is unsatisfactory for aliphatic nitriles.⁶ We are unable to account at this time for this apparent major difference in the applicability of the sodium and lithium reagents.

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⁶G. Hesse and R. Schrödel, Ann. 607, 24 (1957).