

solution of the amide (a) (0.6 g, 3 mmole) and dry triethylamine (0.5 ml, 6 mmole) in dry dichloromethane (10 ml) at 0°C is added a solution of trifluoromethanesulfonic anhydride (0.3 ml, 3 mmole) in dichloromethane (2 ml). The reaction mixture is stirred for 1 hour at the same temperature, then allowed to warm to room temperature and poured into water. The dichloromethane layer is separated and the water layer is extracted three times with dichloromethane (3×25 ml). The organic layers are combined, washed with brine and dried over anhydrous sodium sulfate. Evaporation of the solvent gives the nitrile d, which is purified by flash column chromatography (ethyl acetate : hexane, 1 : 1).

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18. Nitrile (d): TLC ( $R_f$  0.4,  $\text{CHCl}_3$  : MeOH, 10 : 1), NMR (200 MHz,  $\text{CDCl}_3$ ): 8.21 (d, 2H), 7.56 (dd, 2H), 5.19-5.24 (m, 3H), 4.7 (t, 3H), 3.92 (dd, 1H), 3.78 (m, 1H), 2.8 (m, 1H), 2.62 (m, 1H). IR (KBr pellet) 2240  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{14}\text{H}_{15}\text{O}_7\text{N}_3$ : C, 45.52; H, 4.09; N, 11.38. Found: C, 45.48; H, 4.02; N, 11.24.  
Nitrile (e): TLC ( $R_f$  0.8,  $\text{CHCl}_3$  : MeOH, 10 : 1), NMR (200 MHz,  $\text{CDCl}_3$ ): 8.21 (d, 2H), 7.62 (dd, 2H), 5.2-5.24 (m, 3H), 4.61 (m, 1H), 4.5 (m, 1H), 3.5-3.58 (m, 2H), 2.56 (m, 2H), 0.9 (s, 9H), 0.05 (d, 6H). IR (KBr pellet) 2238  $\text{cm}^{-1}$ . Anal. Calcd. for  $\text{C}_{19}\text{H}_{29}\text{SiO}_5\text{N}_3$ : C, 56.15; H, 5.71; N, 10.36. Found: C, 56.15; H, 6.66; N, 10.48.
19. EP 272455 (1987) and JPN 60-233076.

### Partial Reduction of Aromatic Nitriles into Aldehydes by Sodium Diethylpiperidinoaluminumate

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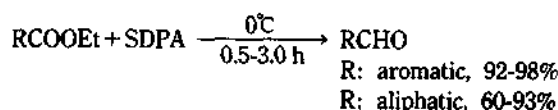
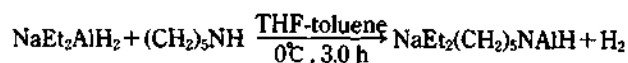
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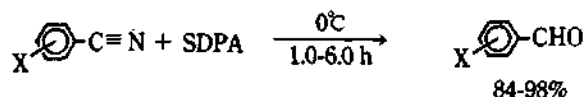
Partial reduction of nitrile function into aldehyde is important in organic synthesis, and many excellent reagents have been reported. Among the metal hydrides, lithium triethoxyaluminum hydride<sup>1</sup> and diisobutylaluminum hydride<sup>2</sup> have been utilized conveniently for this purpose. Recently lithium tris(dialkylamino)aluminum hydride<sup>3</sup> was reported as an attractive selective reducing agent for aromatic nitriles. This prompted us to report our result obtained by the reduction of aromatic nitriles with sodium diethylpiperidinoaluminumate (SDPA)<sup>4</sup>.



SDPA is readily prepared by the reaction of equimolar piperidine with sodium diethyldihydroaluminumate (SDDA) and exhibits excellent reducing ability of carboxylic acid esters to the corresponding aldehydes<sup>4</sup>.



We studied the reducing characteristics of SDPA and found it is also an excellent reducing agent for the partial reduction of aromatic nitriles to the corresponding aldehydes<sup>5</sup>.



The reduction of 4-chlorobenzonitrile is representative. An oven-dried 50 ml flask equipped with a rubber septum on an inlet port and an adaptor connected to a mercury bubbler was flushed with nitrogen and charged with 0.138 g (1.0 mmol) of 4-chlorobenzonitrile in 3.2 ml THF containing mesitylene as an internal standard. The flask was maintained at 0°C in an ice bath and 1.8 ml of 0.85 M SDPA (1.53 mmol) in THF-toluene was injected into the reaction flask with stirring. After 0.5 h, the reaction mixture was hydrolyzed with 10 ml of 2 N  $\text{H}_2\text{SO}_4$  and extracted with 3×10 ml of ether. The ether layer was dried over anhydrous potassium carbonate and analysis by GLC showed a 95% yield of 4-chlorobenzaldehyde. In a large scale reduction, 1.38 g (10 mmol) of 4-chlorobenzonitrile in 32 ml THF was reacted with 18 ml of 0.85 M (15.3 mmol) SDPA at 0°C for 0.5 h. The reaction mixture was hydrolyzed with 100 ml of 2 N  $\text{H}_2\text{SO}_4$  and extracted three times with 50 ml of ether. The ether layer was

**Table 1.** Partial Reduction of Representative Aromatic Nitriles to the Corresponding Aldehydes with SDPA in THF-Toluene at 0°C

Nitrile	Hydride/ compd	Time (h)	Yield of aldehyde <sup>b</sup>
Benzonitrile	1.5	3.0	98
2-methoxybenzonitrile	2.0	6.0	92
3-methoxybenzonitrile	2.0	1.0	94
4-methoxybenzonitrile	1.5	6.0	97
2-tolunitrile	2.0	6.0	90
3-tolunitrile	2.0	6.0	97
4-tolunitrile	2.0	3.0	95
2-chlorobenzonitrile	2.0	3.0	97
3-chlorobenzonitrile	1.5	1.0	98
4-chlorobenzonitrile	1.5	0.5	95(84) <sup>c</sup>
4-bromobenzonitrile	1.5	0.5	84
4-nitrobenzonitrile	1.5	3.0	0
4- <i>N,N</i> -dimethylaminobenzonitrile	2.0	3.0	97
capronitrile	1.5	3.0	0

<sup>a</sup>SDPA was added to nitrile in THF-toluene at 0°C. <sup>b</sup>Yields were estimated by GLC. <sup>c</sup>Isolated yield.

dried over anhydrous potassium carbonate. After removing ether, the residue was dissolved in 30 mL ethanol, and upon addition of water, a crystalline product was appeared. The crude product was sublimed at 55°C under high vacuum<sup>6</sup>, and pure 4-chlorobenzaldehyde (1.18 g, 84%) was obtained: mp. 47-48°C (lit.<sup>7</sup> mp. 47.5°C). The <sup>1</sup>H-NMR spectrum agreed with that of an authentic sample.

The results are summarized in Table 1. As shown in Table 1, all the aromatic nitriles tested gave the corresponding aldehydes almost quantitatively except 4-nitrobenzonitrile.

Apparently the nitro group in the 4-position reacted with SDPA since the reaction mixture immediately turned to dark red which we observed in the reaction of nitrobenzene with SDPA. Electron releasing methyl, methoxy and *N,N*-dimethylamino substituents or electron attracting halogen substituent did not affect the yields of aldehydes. However aromatic nitriles carrying electron attracting substituents generally showed faster rate of reaction. The reduction of capronitrile accompanied a considerable amount (0.35 eq) of hydrogen evolution, and almost no aldehyde was detected. We suspect the  $\alpha$ -hydrogen of capronitrile to be one of the reason. We are going to study more in detail on the reaction of aliphatic nitriles with SDPA. It is interesting to note that  $\text{Li}(\text{R}_2\text{N})_2\text{AlH}$  does not react with aliphatic nitriles<sup>3</sup>.

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