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SELECTIVE REDUCTION OF AROMATIC NITRILES TO ALDEHYDES BY POTASSIUM 9-sec-AMYL-9-BORATABICYCLO[3.3.1]NONANE

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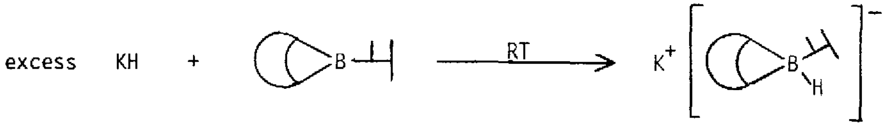
Summary : The title reducing agent (**1**) reduces aromatic nitriles to the corresponding aldehydes in yields of 60-98 %, while aliphatic nitriles being intact.

Transformation of nitriles to aldehydes is of importance in organic synthesis. Numerous methods have been proposed to achieve this objective[1]; however, there have been no report for the selective reduction of only aromatic nitriles to the corresponding aldehydes in the presence of aliphatic nitriles.

In the course of a systematic study of the reducing power of potassium 9-sec-amyl-9-boratabicyclo[3.3.1]nonane (K 9-sec-Am-9-BBNH, **1**) toward selected organic compounds containing representative functional groups[2], we found that the reagent possesses an unique reducing characteristics, showing excellent chemo- and stereoselectivities[3]. Excess **1** in THF does not reduce aliphatic nitriles even at room temperature. However, unexpectedly, the reaction of aromatic nitriles with the reagent results in relatively fast utilization of 1 equiv of hydride, followed by very slow utilization of a second equivalent of hydride. This remarkable feature in the rate of reaction suggested the possibility of achieving the selective reduction of aromatic nitriles in the presence of aliphatic nitriles under practical conditions. In this communication, we now report such selective conversion of aromatic nitriles to the corresponding aldehydes by using a 9-BBN derivative.

The reducing agent, K 9-sec-Am-9-BBNH, is readily prepared by treating 9-sec-Am-9-BBN with excess KH in THF (eq 1)[3]. 9-sec-Am-9-BBN is readily prepared by hydroborating 2-methyl-2-butene with 9-BBN[3].



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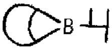
( ≡ 9-sec-amyl-9-borabicyclo[3.3.1]nonane ≡ 9-sec-Am-9-BBN)

The reagent reduces unsubstituted aromatic nitriles, such as benzo- and naphthonitriles, to the corresponding aldehydes in yields of 91-98 %, as shown in Table 1, in approximately 24 h at room temperature. Dinitriles, such as phthalo- and terephthalonitriles, are reduced to dialdehydes in yields of 64-97 %. Derivatives are readily accommodated. Thus, p-carboxybenzonitrile is reduced to p-carboxybenzaldehyde in an essentially quantitative yield. 2,4-Dichlorobenzonitriles also works well to give a 80 % yield. Examining the results more closely, a sig-

Table 1. Yields of Aldehydes in the Reduction of Representative Aromatic Nitriles with Potassium 9-sec-Amyl-9-boratabicyclo[3.3.1]nonane in Tetrahydrofuran at Room Temperature[a]

Compound	Yield of aldehydes (%)[b]
benzonitrile	98 (88)[c]
1-naphthonitrile	91
phthalonitrile[d]	64
terephthalonitrile[d]	97
p-carboxybenzonitrile[d]	98
2,4-dichlorobenzonitrile	80
o-tolunitrile	60
m-tolunitrile	97 (89)[c]
p-tolunitrile	83
2-cyanopyridine	73
3-cyanopyridine	96
4-cyanopyridine	65

a) Reacted with 10 % excess **1** (1.1 equiv for mononitrile and 2.2 equiv for dinitrile) for 24 h at room temperature. b) Analysis with (2,4-dinitrophenyl)hydrazine. c) Yields are based on the analytically pure aldehydes isolated after evaporation of solvent, following treatment of the bisulfite adduct with formaldehyde[4]. d) 2.2 equiv of **1** utilized.

nificant influence of the position of substituents upon the yield appears to exist. Thus, the yields realized for the tolunitriles (i.e., o-, m- and p-tolunitriles) are significantly varied with the position of substituents on the benzene ring from 60 to 97 %. Similar results are also appeared in the cyanopyridines (i.e., 2-, 3- and 4-cyanopyridines); the yields are varied from 65 to 96 %.

As mentioned above, the reagent, **1**, does not reduce aliphatic nitriles; however, aromatic nitriles are reduced to the aldehyde stages at a relatively fast rate. We attempted to reduce aromatic nitriles to the corresponding aldehydes selectively in the presence of aliphatic nitriles intact. Indeed, as shown in Table 2, we achieved up to 91-93 % reduction of aromatic nitriles in mixtures with aliphatic nitriles, with only minor reduction of the aliphatic nitriles, with a limiting amount of the reagent.

The following procedure for the reduction of m-tolunitrile is representative. An oven-dried 200-mL flask, equipped with a side arm, a condenser, and an adaptor connected to a mercury bubbler, was flushed with nitrogen and charged with 6.21 g (53 mmol) of m-tolunitrile and 43 mL of 1.35 M solution of **1** (58 mmol, 10 % excess) in THF. The reaction mixture was stirred for 24 h at room temperature. Analysis of an aliquot with (2,4-dinitrophenyl)hydrazine yielded 98 % of the corresponding aldehyde.

The rest of the reaction mixture (50 mmol) was hydrolyzed with 30 mL of 2 N HCl for 3 h at room temperature. The mixture was then saturated with sodium chloride and the separated organic layer was subjected to the sodium bisulfite isolation procedure[4]. Thus, the separated organic layer was poured into 75 mL of a saturated aqueous sodium bisulfite solution. The mixture was

Table 2. Selective Reduction of Aromatic Nitrile in the Presence of Aliphatic Nitrile with Potassium 9-sec-Amyl-9-boratabicyclo[3.3.1]nonane in Tetrahydrofuran at Room Temperature[a,b]

Compound used	Product	Mol %[c]
benzonitrile + caprylonitrile	benzaldehyde	91
	benzonitrile	2
	caprylic aldehyde	0
	caprylonitrile	99
terephthalonitrile + decanenitrile	terephthalaldehyde	93
	terephthalonitrile	0
	decyl aldehyde	0
	decanenitrile	98

a) 1.1 equiv of the reagent per mixture of 1 equiv in each of the compounds was utilized.
b) Reacted for 24 h at room temperature. c) Determined by GC analysis with an internal standard and authentic samples.

stirred for 1 h and cooled in an ice-water bath to ensure complete crystallization of the bisulfite adduct, which was then collected by filtration and washed with 3 x 25 mL of pentane and dried. The solid adduct was placed in 40 mL of water and then 50 mL of THF and 8 mL of a 37 % formaldehyde solution were added. The mixture was stirred for 1 h and saturated with magnesium sulfate heptahydrate. The organic layer was separated and dried. Evaporation of all volatiles gave analytically pure m-tolualdehyde (5.35 g, 89 %).

The following procedure for the competitive reaction between benzonitrile and caprylonitrile is representative. In the usual setup, a 50-mL flask was charged with 0.41 g of benzonitrile (4 mmol), 0.50 g of caprylonitrile (4 mmol), and 3.26 mL of 1.35 M **1** (4.4 mmol) in THF. The reaction mixture was stirred for 24 h at room temperature. The reaction was then quenched with water, and n-dodecane as an internal standard and 4 mL of ether were added. A part of organic layer was analyzed by GC for nitriles and n-dodecane. The rest of organic layer was then hydrolyzed with 2 N HCl and the separated organic layer was subjected to GC analysis for aldehydes and n-dodecane. The combined GC analysis indicated a 91 % yield of benzaldehyde and 99 % of caprylonitrile unreacted.

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