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EXCEPTIONALLY FACILE REDUCTION OF CARBOXYLIC ACID SALTS TO ALDEHYDES BY 9-BORABICYCLO[3.3.1]NONANE

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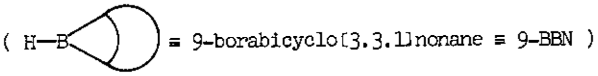
Abstract - Both sodium and lithium salts of carboxylic acids in the presence of 2 equiv of 9-borabicyclo[3.3.1]nonane(9-BBN) are readily converted to the aldehydes in approximately 1-3 h at room temperature in high yields. Thus, simple aliphatic carboxylic acid salts, such as butyric, hexanoic, decanoic, stearic, isobutyric, isopentanoic, pivalic, cyclopropanecarboxylic, and cyclohexanecarboxylic acid salts, readily undergo the reaction to aldehydes in yields of 84-99%. Derivative, such as diphenylacetic acid salts, undergoes the reaction in almost quantitative yields. Even dicarboxylic acid salts, such as α-camphoric and 1,10-decanedicarboxylic acid salts, work equally well. The yields of aromatic carboxylic acid salts are variable ranged from 54 to 83% except for the case of terephthalic acid salts being 99%.

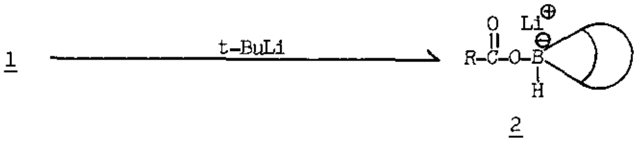
Very recently, we have reported that carboxylic acid salts can be converted to the corresponding aldehydes in high yields using excess thexylbromoborane-methyl sulfide through substitution of the bromo group of reagent with carboxylate followed by reduction[1]. This apparently first development encouraged us to explore a new methodology for such direct conversion using a commercially available 9-borabicyclo[3.3.1]nonane(9-BBN). Herein, we now describe such an equally facile conversion of carboxylic acid salts to the corresponding aldehydes by using 9-BBN.

The acyloxy moiety of acyloxy-9-BBN (1), formed from the reaction of carboxylic acid and 9-BBN with immediate evolution of hydrogen, is readily converted to the aldehyde stage through stepwise treatment of 1 with tert-butyllithium and 9-BBN[2](eqs 1, 2, and 4). If a carboxylate and 9-BBN form an ate complex (eq 3), which is the same compound (2) formed by treatment of acyloxy-9-BBN with tert-butyllithium (eq 2), we can expect that in the presence of another equiv of 9-BBN the system follows the exactly same reduction pathway as the case of reduction of carboxylic acid through stepwise treatment of acyloxy-9-BBN with tert-butyllithium and 9-BBN[2].

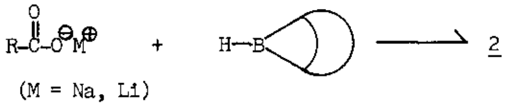
Actually, this system is in equilibrium, in which the acyloxy group of ate complex thus formed is readily transformed into the corresponding aldehyde stage in the presence of excess 9-BBN. In fact, we found that this system achieves a nice conversion of carboxylic acid salts to the aldehyde stage. The reduction proceeds readily as the mixture of a carboxylate and 2 equiv of 9-BBN, providing a simple procedure with high yields of aldehydes. This procedure is really promising. Consequently, we examined both sodium and lithium salts of various carboxylic acids and the results are summarized in Table 1.

(1)

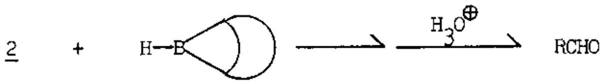

(H—B = 9-borabicyclo[3.3.1]nonane ≡ 9-BBN)



(2)

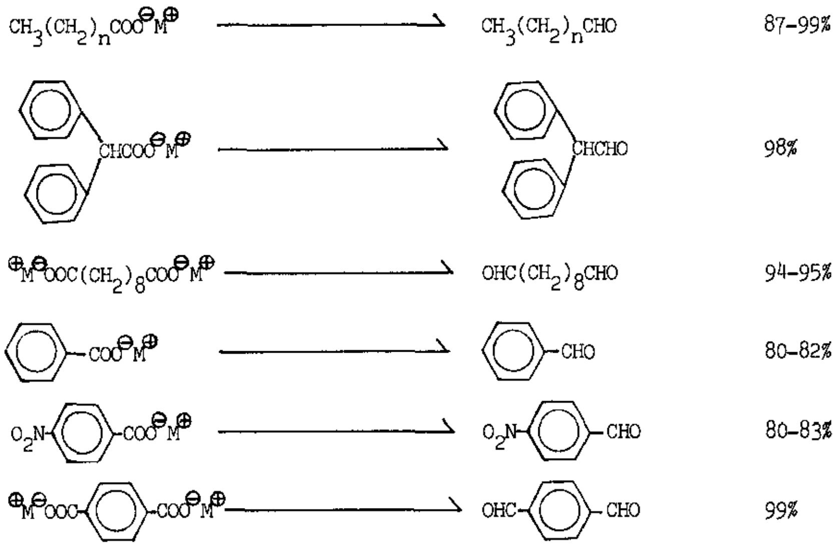


(3)



(4)

Both sodium and lithium salts of most aliphatic carboxylic acid, such as salts of butyric, hexanoic, decanoic, stearic, isobutyric, isopentanoic, and pivalic acids, are readily converted to the corresponding aldehydes by this system in approximately 1 h at room temperature. The yields of aldehydes from the lithium salts are essentially quantitative, whereas the yields from the corresponding sodium salts are in the range of 87-99%, a little lower than those from the lithium salts probably due to the relatively lower solubility of sodium salts in THF solvent. Derivatives, such as both sodium and lithium salts of diphenylacetic acid, also undergo the reaction well in yields of 98%. The yields of aldehydes from alicyclic carboxylic acid salts, such as cyclopropanecarboxylic and cyclohexanecarboxylic acid salts, are in the range of 84-92%. The halogeno derivatives, such as salts of chloro- and bromoacetic acids, and 6-bromohexanoic acid, provide the corresponding haloalkanals



in yields of 65-84%. Dicarboxylic acid salts such as α-camphoric and 1,10-decanedicarboxylic acid salts are also converted readily to dialdehydes in yields of 88-95%.

The reduction of aromatic carboxylic acid salts by this system requires 3 h at room temperature and the yields vary with the substituents on benzene ring. Thus, in the case of aromatic acid salts bearing an electron-releasing substituent such as p-methyl- and p-methoxybenzoic acid salts, the yields are around 40% for the sodium salts and around 60% for the lithium salts. However, aromatic acid salts bearing an electron-withdrawing substituent such as p-chloro- and p-nitrobenzoic acid salts provide the much higher yields of the corresponding aldehydes (70-83%). Finally, both disodium and dilithium salts of aromatic dicarboxylic acid, such as terephthalic acid salts, are readily converted to the corresponding dialdehyde in essentially quantitative yields.

The aldehyde products of relatively low boiling point (less than 200°C) are readily isolable on distillation after hydrolysis[3] (i.e., 83% for hexanal), whereas the products of higher boiling point can be isolated readily by the sodium bisulfite procedure[4] in a pure form (i.e., 91% for stearaldehyde, 90% for diphenylacetaldehyde, and 90% for 1,10-decanal).

Table 1. Yields of Aldehydes in the Reduction of Representative Sodium and Lithium Salts Carboxylic Acids by 9-Borabicyclo[3.3.1]nonane in Tetrahydrofuran at Room Temperature[a]

Acid salt	Yield of aldehyde by analysis with 2,4-dinitrophenylhydrazine (%)	
	Na Salt	Li Salt
butyric	89[b]	97
hexanoic	87[b]	99(83)[c]
decanoic	88	98
stearic	99	99(91)[d]
isobutyric	91	99
isopentanoic	88	92
pivalic	93[e]	-
diphenylacetic	98(90)[d]	98
cyclopropanecarboxylic	88	84
cyclohexanecarboxylic	90	92
chloroacetic	74	72
bromoacetic	69	65
6-bromohexanoic	78	84
α-camphoric	88	89
1,10-decanecarboxylic	94	95(90)[d]
benzoic	82	80
p-methylbenzoic	44	60
p-methoxybenzoic	38	66
p-chlorobenzoic	70	75
p-nitrobenzoic	83	80
terephthalic	99	99

a) Reacted with 2 equiv of 9-BBN (2 equiv for monocarboxylic and 4 equiv for dicarboxylic acid salts) for 1 h with aliphatic and for 3 h with aromatic carboxylic acid salts, both at room temperature. b) Reacted for 0.5 h. c) An isolated yield on distillation after hydrolysis[3].
d) Yields are based on the analytically pure products isolate after evaporation of solvent, following treatment of the bisulfite adduct with formaldehyde[4]. e) Reacted for 3 h.

The following procedure for the reduction of sodium diphenylacetate was used for quantitative analysis of yields. An oven-dried 50-ml flask, fitted a sidearm and a bent adaptor connected to a mercury bubbler, was charged with 0.70 g (3 mmol) of sodium diphenylacetate. A 0.5 M solution 9-BBN 12 ml in THF (6 mmol) was injected, and the slurry was stirred for 1 h at room temperature. Analysis with 2,4-dinitrophenylhydrazine indicated a yield of 98%.

The following procedure was used for a larger scale reaction. In the assembly previously described, 11.7 g of sodium diphenylacetate (50 mmol) was added. A 0.5 M 9-BBN solution 200 ml in THF (100 mmol) was injected and the slurry was stirred for 1 h at room temperature. The reaction mixture was hydrolyzed with 30 ml of 2 N HCl solution for 1 h at room temperature and then saturated with sodium chloride. The separated organic layer was poured into 75 ml of a saturated aqueous sodium bisulfite solution[4]. The mixture was stirred for 1 h, by which time the crystalline bisulfite adduct of diphenylacetaldehyde has precipitated. The solution was 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 heated to 90-95°C for 1 h with stirring and cooled to room temperature followed by saturation with magnesium sulfate heptahydrate. The organic layer was separated and dried. Evaporation of volatile gave 8.82 g of analytically pure diphenylacetaldehyde (90%) : n_D^{20} 1.5892.

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1. J.S. Cha, J.E. Kim, and K.W. Lee, J. Org. Chem., 1987, 52, 5030.
2. J.S. Cha, J.E. Kim, M.S. Yoon, and Y.S. Kim, Tetrahedron Lett., 1987, in press.
3. The typical procedure is as follows : The reaction mixture (50 mmol) was hydrolyzed with 30 ml of 2 N HCl for 1 h and then saturaed with sodium chloride. The separated organic layer was stirred vigorously over excess anhydrous magnesium sulfate overnight and subjected to fractional distillation.
4. (a) H.C. Brown, J.S. Cha, B. Nazer, and N.M. Yoon, J. Am. Chem. Soc., 1984, 106, 8001.
   (b) H.C. Brown, J.S. Cha, N.M. Yoon, and B. Nazer, J. Org. Chem., 1987, 52, 5400.

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