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RAPID REDUCTION OF CARBOXYLIC ACID SALTS WITH BORANE IN TETRAHYDROFURAN.

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Summary: Carboxylic acid salts are rapidly reduced to the corresponding alcohols with two molar equivalents of borane in THF. A possible mechanism via acyloxyborane is presented.

It is well established that carboxylic acids are rapidly reduced to the corresponding alcohols with borane via acyloxyborane.[1-3]

$$\text{RCOOH} \quad + \quad \text{BH}_3 \xrightarrow[\text{THF}]{} \text{RCOOBH}_2 \longrightarrow \text{RCH}_2\text{OB}{<}$$

On the other hand, the reduction of carboxylic acid salts has been a rather neglected area of research,[4] since a rather sluggish reaction with approximately one molar equivalent of borane was observed some time ago.[1]

Recently we found that acyloxyborohydrides, produced from carboxylic acids and sodium borohydride, react with dimethyl sulfate or Lewis acids to give excellent yields of the corresponding alcohols.[5] Therefore we decided to clarify more thoroughly the reaction of carboxylic acid salts with borane, since carboxylic acid salts are expected to form indentical acyloxyborohydrides with borane and borane itself is a Lewis acid.

Sodium benzoate was chosen as a representative salt. It was treated with 3, 2, 1.33, 1, and 0.67 molar equivalents of BH_3 in THF at room temperature. The results are summarized in Fig. 1. The yields of benzyl alcohol were estimated by glpc.

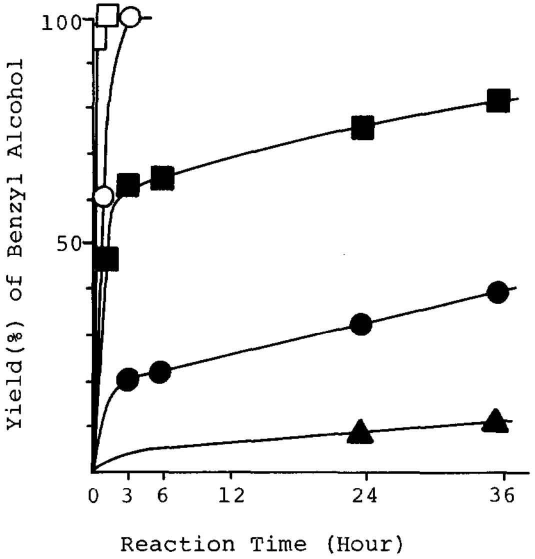


Fig.1. Reduction of Sodium Benzoate with Borane in Tetrahydrofuran at Room Temperature.

C_6H_5COONa/BH_3: 1/3(□), 1/2(○), 1/1.33(■), 1/1(●), 1/0.67(▲)

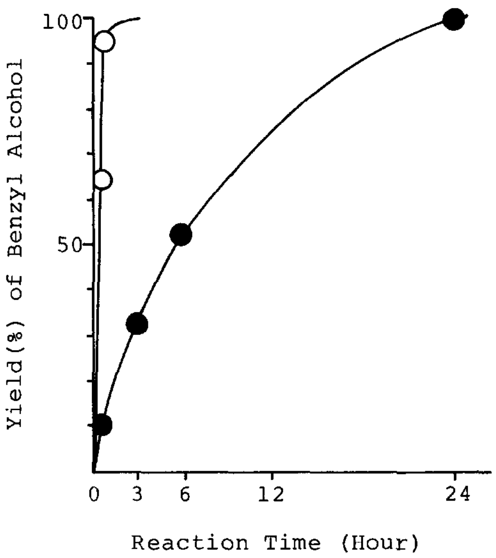


Fig.2. Reduction of Sodium Benzoate with Borane and Borane Methyl sulfide in Tetrahydrofuran at Room Temperature.

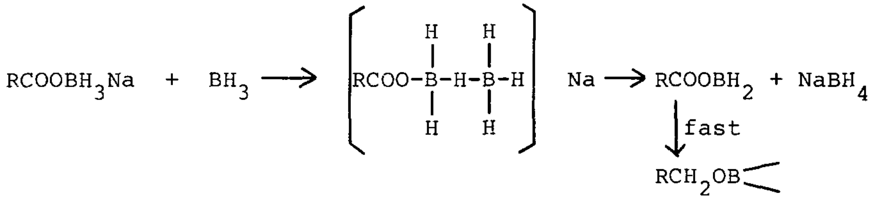
C_6H_5COONa/BH_3(○) or BMS(●) : 1/3

As shown in Fig. 1, sodium benzoate was reduced rapidly in 3 hr, with two molar equivalents of borane; with 1.33 molar equivalents, two thirds of the reduction was fast; with one molar equivalent of BH_3, the reduction was much slower, as observed earlier.

Sodium benzoate was also treated with borane dimethyl sulfide (BMS) in place of BH_3 (Fig. 2). The reduction was much slower, requiring approximately 24 hr., in contrast to the rapid reduction with BH_3 in 1 hr., both experiments with three molar equivalents of BMS and BH_3 respectively.

These results suggest the following mechanism.

$$\mathrm{RCOONa} \quad + \quad \mathrm{BH_3} \longrightarrow \mathrm{RCOOBH_3Na} \qquad (1)$$



$$\mathrm{RCOOBH_3Na} + \mathrm{BH_3} \longrightarrow \left[\mathrm{RCOO{-}\overset{H}{\underset{H}{B}}{-}H{-}\overset{H}{\underset{H}{B}}{-}H}\right]\mathrm{Na} \longrightarrow \mathrm{RCOOBH_2} + \mathrm{NaBH_4} \qquad (2)$$

$$\mathrm{RCOOBH_2} \xrightarrow{\text{fast}} \mathrm{RCH_2OB}{<}$$

This mechanism is consistent with the requirement for two molar equivalents of BH_3 per mole of salt to achieve the rapid reduction, and the slower reduction with BMS. In the latter case the equilibrium constant of (1) is expected to be smaller with BMS than with BH_3. Furthermore hydride transfer in (2) is also expected to be slower with BMS than with BH_3.

Table 1. Reduction of Carboxylic Acid Salts with Two Molar Equivalents of Borane in Tetrahydrofuran at Room Temperature.

	Yields of Alcohols (%)[a]					
Salts \ Time hr.	0.25	0.5	1.0	3.0	6.0	10.0
$C_5H_{11}COONa$	90	100				
t-C_4H_9COONa	89	100				
C_6H_5COONa	60	78	93	100		
o-ClC_6H_4COONa		46	81	92	95	100

a : Yields were estimated by glpc.

Three additional carboxylic acid salts were reduced with two molar equivalents of BH_3, in order to test the generality of the reduction. As shown in Table I, the two aliphatic acid salts, sodium caproate and sodium pivaloate, underwent reduction quantitatively in 30 minutes, whereas sodium o-chlorobenzoate exhibited somewhat slower rate than that of sodium benzoate. However, even here a 100% yield was realized in 10 hr.

The reduction of sodium benzoate is illustrated as a representative procedure. Into a oven-dried 50 ml flask, equipped with a side arm fitted with a rubber septum, a magnetic stirring bar, and a reflux condenser connected to a gas buret were introduced 0.7205g (5 mmol) of sodium benzoate, THF (5 ml) and diphenyl ether in THF (2.5 mmol, 5 ml) to serve as an internal standard for glpc analysis. The reaction was started by the addition of BH_3-THF (10 mmol, 10 ml). The reaction mixture was stirred at room temperature under a nitrogen atmosphere. After 3 hr, an aliquot was withdrawn, hydrolyzed with d-H_2SO_4, made alkaline with d-NaOH, extracted with ethyl ether and the organic layer was analyzed by glpc. The analysis indicated the formation of benzyl alcohol in 100% yield.

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