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# Acetoxyborohydride: A Simple Selective Hydroborating Agent

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Abstract: Acetoxyborohydride ($CH_3COO\bar{B}H_3$) hydroborates olefins in the presence of some reducible functional groups.

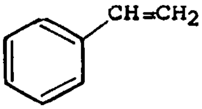
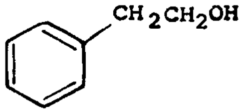
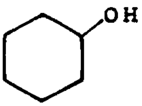
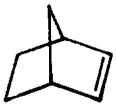
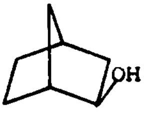
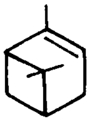
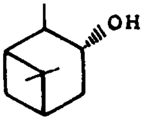
In the course of our investigation on the carbonylation of organometallics,[1] we have observed that a mixture of mercuric acetate (1mole) and sodium borohydride (2mole) in anhydrous tetrahydrofuran (THF) hydroborates olefins. The corresponding alcohols can be isolated in good yields after oxidation with $H_2O_2/\bar{O}H$ (Table). However, the hydroboration is relatively slow and only one equivalent of olefin reacts in 12h at room temperature. Presumably, the reaction of sodium borohydride with mercuric acetate would produce acetoxyborohydride species.[2]

$$Hg(OOCCH_3)_2 + 2NaBH_4 \xrightarrow{THF} 2CH_3COO\bar{B}H_3 + 2Na^+ + H_2 + Hg$$

We wish to report that such acetoxyborohydride species which can also be prepared readily by the addition of acetic acid (1mole) to $NaBH_4$ (1mole) in THF,[3] is useful for applications in the selective hydroboration of alkenes in the presence of some reducible functional groups and also promising for the preparation and utility of mono- and dialkyl organoboron species.

It has been reported that addition of acetic acid (1mole) into a mixture of olefin (3mole) and $NaBH_4$ (1mole) in THF at 15-20°C for 1h followed by further stirring for 2h at room temperature gives $R_3B$ in the case of terminal olefins.[4] However, we have observed that if 1-decene is added after the addition of acetic acid (20mmol) into $NaBH_4$ (20mmol) in THF (60ml) at 0°C for 1h and further stirring the reaction mixture for 1h at room temperature, only one equivalent of 1-decene (20mmol) reacts in 12h at room temperature (Table). Clearly, complexation of the borane species with the acetate anion reduces the rate of hydroboration.

Table : Hydroboration-Oxidation of Alkenes[a,b]

| Alkene | Product | Yield[c] [%] Method A[d] | Method B[e] |
|---|---|---|---|
| $CH_3(CH_2)_7CH=CH_2$ | $CH_3(CH_2)_8CH_2OH$ | 70 | 76 |
|  |  | 82[f] | 89[f] |
|  |  | 80 | 85 |
|  |  | 79 | 84 |
|  |  | 70 | 72 |
| $CH_2=CH-(CH_2)_8COOCH_3$ | $HO-CH_2CH_2(CH_2)_8COOCH_3$ | - | 73[g] |

[a] $Hg(OAc)_2$ used is of Reagent Grade. Acetic acid was distilled after adding calculated amount of acetic anhydride to remove water. THF was distilled over $LiAlH_4$ or benzophenone-sodium. Sodium borohydride supplied by Fluka, Switzerland and the sample supplied by LOBA-CHEMIE, India, give identical results.

[b] Acetoxyborohydride (20mmol) was prepared by slow addition of $Hg(OAc)_2$ (10mmol) or $CH_3COOH$ (20mmol) to the suspension of $NaBH_4$ (20mmol) in THF (60ml) at 0°C for 1h. The reaction mixture was brought to room temperature and the alkene (20mmol) was added. The contents were further stirred for 12h before oxidation.

[c] Yields are of isolated and distilled products. The products are identified by the spectral data (ir, $^1H$-NMR and $^{13}C$-NMR) and comparison with the data reported in the literature.

[d] Method A: Hydroboration with $Hg(OAc)_2$ - $NaBH_4$ and oxidation with $H_2O_2/NaOH$.

[e] Method B: Hydroboration with $CH_3COOH$-$NaBH_4$ and oxidation with $H_2O_2/NaOH$.

[f] The isomeric 1-phenylethanol is present to the extent of 8%. Products in other cases contain only small amount (<5%) of the isomeric alcohol (if any).

[g] Oxidation with $H_2O_2/NaOOCCH_3$.

Similar slow hydroboration is well known in the case of amine-borane complexes.[5] However, the hydroboration with amine-borane complexes can be achieved only at elevated temperatures. Although the hydroboration of alkenes with acetoxyborohydride is slow, it occurs to significant extent at room temperature. This should make acetoxyborohydride a suitable reagent for the hydroboration of olefins in the presence of functional groups. In order to examine this possibility, we mixed 1-decene (10mmol) with 10mmol of cyclohexanone, benzonitrile, ethylbenzoate and benzamide in THF (60ml) in individual runs in the reaction with acetoxyborohydride (10mmol) at room temperature for 12h. Hydroboration of 1-decene takes place without the reduction of ethylbenzoate and benzamide. Also, cyclohexanone is completely reduced to cyclohexanol and benzonitrile is partly reduced to benzylamine ($\sim$ 50%) along with complete hydroboration of 1-decene. Under these conditions methyl-10-undecenoate gives 11-hydroxyundecanoate (Table) after oxidation with $NaOOCCH_3/H_2O_2$ and the corresponding 1,11-diol is not formed.

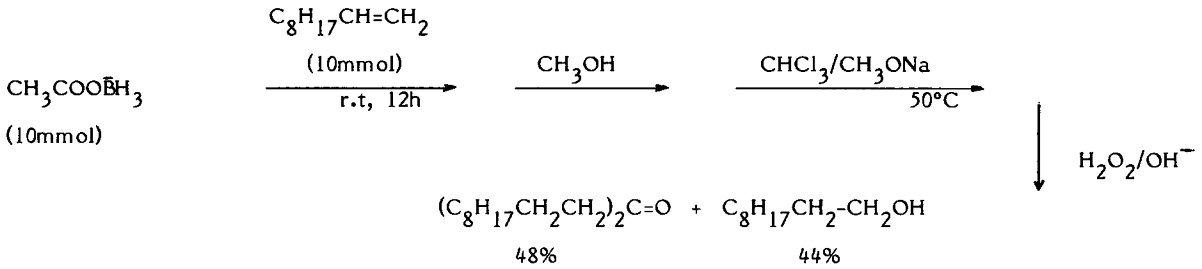
Similar selectivities have been also observed with $BH_3$-THF under controlled conditions.[6] However, it should be pointed out that whereas in the present method the ester reduction does not take place inspite of the presence of two equivalents of "excess" B-H bonds, in the case of $BH_3$-THF excess reagent should be avoided.[6]

The most interesting and important application of the reagent system is the selective hydroboration of the olefin when it is present in a molecule along with the carboxylic acid group (eg.10-undecenoic acid). As $BH_3$-THF reduces the carboxylic acid group faster than the hydroboration of olefin, it is necessary to protect the carboxylic group by esterification.[6] The alternate method recommended for the direct selective hydroboration of olefin in the presence of carboxylic acid group requires 2 equivalents of disiamylborane which serves as both the protecting and hydroborating agent because of steric hindrance.[7,8] However, we have found that this goal can be readily achieved by adding 10-undecenoic acid (10mmol) into $NaBH_4$ (10mmol) in THF (60ml) at 0°C for 1h and further stirring the reaction mixture for 12h at room temperature. After oxidation of the reaction mixture with $NaOH/H_2O_2$ and neutralization with 2N HCl, 11-hydroxyundecanoic acid can be isolated in 85% yield and the corresponding 1,11-diol is not formed.

$$CH_2{=}CH\text{-}(CH_2)_8COOH \xrightarrow[THF]{NaBH_4} \xrightarrow{H_2O_2/OH^-} \xrightarrow{H^+} HO\text{-}CH_2\text{-}CH_2\text{-}(CH_2)_8COOH$$

Since the hydroboration with acetoxyborohydride is relatively slow the organoboron species formed using one equivalent of olefin may be probably the complexed "$RBH_2$" and/or "$R_2BH$" species. In order to examine this possibility we methanolysed the hydroboration product of 1-decene (10mmol) and acetoxyborohydride (10mmol) using the calculated amount of methanol. Chloroform (40mmol) was added followed by slow addition of $NaOCH_3$ (40mmol) in portions at 50°C for 1h using a solid addition flask under nitrogen atmosphere. After further stirring the reaction mixture for 1h at 50°C followed by oxidation with $NaOH/H_2O_2$, di-1-decylketone (48%) and 1-decanol (44%) (Scheme 1) were isolated. No trialkylcarbinol was present.

Scheme 1



$$\underset{(10mmol)}{CH_3COO\bar{B}H_3} \xrightarrow[\text{r.t, 12h}]{\overset{C_8H_{17}CH=CH_2}{(10mmol)}} \xrightarrow{CH_3OH} \xrightarrow[50°C]{CHCl_3/CH_3ONa} \xrightarrow{H_2O_2/OH^-} \underset{48\%}{(C_8H_{17}CH_2CH_2)_2C=O} + \underset{44\%}{C_8H_{17}CH_2\text{-}CH_2OH}$$

The above carbenoid reaction is similar to the "DCME" reaction using dichloromethylmethyl ether and lithium triethylcarboxide which is known to give trialkylcarbinol from $R_3B$, dialkylketone from $R_2BOCH_3$ and R-OH from $RB(OCH_3)_2$ after oxidation.[6] Consequently, we conclude that the hydroboration of 1-decene with $CH_3COO\bar{B}H_3$ gives not only "$RBH_2$" species but also some "$R_2BH$" species under the present reaction conditions.

We are currently investigating the possibility of synthesising "$RBH_2$" and "$R_2BH$" species and the application of these species in organic synthesis.

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