Reactions of Sodium Borohydride in Acidic Media.[1] Selective Reduction of Aldehydes with Sodium Triacetoxyborohydride

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Summary Aldehydes, but not ketones, are smoothly reduced to alcohols with sodium triacetoxyborohydride, prepared from sodium borohydride and acetic acid in benzene.

Although aldehydes are generally reduced more rapidly than ketones by alkali metal borohydrides[2,3] and aluminohydrides[3,4] and di-borane,[5,6] the absolute rates of reduction are too fast to take advantage of the inherent relative rate differences between aldehydes and ketones, thereby making the selective reduction of aldehydes impractical.

Our recent report[1] that aldehydes can be generated from carboxylic acids with sodium borohydride (leading to a new alkylation of amines[1,7]) suggested that aldehydes and ketones are in fact reduced relatively slowly by sodium borohydride in carboxylic acid media, and that a practical selective reduction of aldehydes was feasible.

Thus, treating a benzene suspension of sodium borohydride (4 equiv.) with glacial acetic acid (3·25 equiv.) and refluxing the mixture for 15 min under nitrogen, after the initial rapid gas evolution subsided (*ca.* 3 mol of H_2 liberated), gave a clear solution of $NaBH(OAc)_3$.[8] To this solution of $NaBH(OAc)_3$ (0·027 mol) was added an equimolar mixture of benzaldehyde and acetophenone (0·007 mol each), and the mixture was refluxed for 1 h. Workup gave a mixture (87% recovery) of benzyl alcohol, acetophenone, and α-phenethyl alcohol, in the proportions (n.m.r.) 100:92:8, indicating complete reduction of benzaldehyde but <10% reduction of acetophenone under the extreme conditions of excess of $NaBH(OAc)_3$ in refluxing benzene.

A similar reaction with a mixture of phenylacetaldehyde and dibenzyl ketone gave a mixture (90% yield) containing (n.m.r.) only β-phenethyl alcohol and recovered dibenzyl ketone.

On refluxing the benzene solution of $NaBH(OAc)_3$ for 6 h, then adding benzaldehyde, only 8% reduction to benzyl alcohol is found. This is consistent with the self-reduction of $NaBH(OAc)_3$ to ethanol *via* acetaldehyde as proposed[1] for the amine alkylation sequence involving $NaBH(OAc)_3$.

The remarkably mild reducing characteristics of $NaBH(OAc)_3$ may be attributed both to the bulky nature of the reagent and to the inductive electron-withdrawing ability of the three acetoxy groups (σ_I 0·39)[9] which stabilize the boron–hydrogen bond.

Although acyloxyborohydride species have been sporadically mentioned in the literature[5,8,10] the synthetic potential for these reagents has never been realized.

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