Trimethylamine–Borane Bromide as Alternative Reagent for Reductive Bromation of Aromatic Carbonyl Compounds

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The reaction of bromine with aromatic carbonyl compounds and trimethylamine–borane in chloroform leads to benzyl bromides.

The commercially available trimethylamine–borane complex (TMAB) has potential for becoming especially useful owing to its stability. Unfortunately the hydroboration of alkenes and the reduction of carbonyl compounds with TMAB in neutral solvents was found to be quite slow.[1] In the presence of a protic or Lewis acid (BF_3), TMAB was found to be a much more effective reducing reagent.[1] We describe now a new application of this reagent for the direct synthesis of benzyl bromides from aromatic aldehydes and ketones.

It is known that trimethylamine reacts exothermically with bromine. We therefore added bromine to the reaction mixture of a carbonyl compound and TMAB and found that this was a very efficient process for the induction of reduction. Aliphatic aldehydes and ketones are reduced to alcohols at room temperature. However, in the case of aromatic compounds, the alkoxyboranes are converted rapidly into the corresponding benzyl bromides (equation 1).

$$\underset{(\mathbf{1})}{\text{Ar–CO–R}} + \text{Me}_3\text{NBH}_3 \xrightarrow{\text{Br}_2} \underset{(\mathbf{2})}{\text{Ar–CHBr–R}} \tag{1}$$

$$\text{Me}_3\text{NBH}_3 \xrightarrow{\text{Br}_2} \underset{(x+y=3)}{\text{Me}_3\text{NBH}_x\text{Br}_y} \tag{2}$$

In order to obtain the optimum yield of the bromides it was necessary that the temperature of the reduction reaction be carefully controlled to reduce the formation of trimethylamine bromoboranes (equation 2).[2]

Table 1. Preparation of benzyl bromides.

	Carbonyl compound		Yield (%) of (**2**)	Reaction time/min	Br_2 (mmol)[a]
	Ar	R			
(**1a**)	Ph	H	85	15	2
(**1b**)	3-MeC_6H_4	H	92	2	2
(**1c**)	4-$MeOC_6H_4$	H	86	2	1.2
(**1d**)	4-$NO_2C_6H_4$	H	25[b]	60	2
(**1e**)	Ph	Me	84	2	2
(**1f**)	4-ClC_6H_4	Me	95	60	2

[a] For 1 mmol of carbonyl compound. [b] After recrystallisation from ethanol.

As can be seen from Table 1, the yields are good. However it is apparent that a strong electron withdrawing substituent on the benzene ring tends to decrease the amount of bromination.

A typical procedure consists of dropwise addition of bromine (1.2—2.0 mmol) to a solution of carbonyl compound (1 mmol) and TMAB (1 mmol) in dry chloroform. The reaction was quite exothermic and the internal reaction temperature was maintained at 0—5 °C. After 2—60 min of stirring at 50 °C, the solution was treated with water. The chloroform was removed under reduced pressure to leave a residue which was taken up in hexane or diethyl ether [for (**1d**)]. Evaporation *in vacuo* gave the desired pure benzyl bromide (95% purity).

In conclusion, this one-pot procedure offers a simple and efficient method for the preparation of benzyl bromides. To our knowledge, there is only one method reported in the literature[3] for the direct conversion of (**1**) to (**2**).

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References

1 W. M. Jones, *J. Am. Chem. Soc.*, 1960, **82**, 2528; H. C. Brown and L. T. Muray, *Inorg. Chem.*, 1984, **23**, 2746.
2 H. Noth and H. Beyer, *Chem. Ber.*, 1960, **93**, 2251.
3 J. M. Aizpurua and C. Palomo, *Tetrahedron Lett.*, 1984, **25**, 1103.