Monatshefte für Chemie 136, 2041–2043 (2005)
DOI 10.1007/s00706-005-0376-x

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Sodium Borohydride – Ammonium Carbonate: An Effective Reducing System for Aldehydes and Ketones

Farajollah Mohanazadeh[1,*], **Mostafa Hosini**[2],
and **Mahmoud Tajbakhsh**[2]

[1] Institute of Industrial Chemistry, Iranian Research Organization for Science and Technology, Tehran, Iran
[2] Institute of Chemistry, Mazandaran University, Babolsar, Iran

Received March 14, 2005; accepted (revised) April 24, 2005

Summary. Reduction of aldehydes and ketones to the corresponding alcohols was achieved in a simple procedure using the system sodium borohydride and ammonium carbonate. This system needs lower excesses of reducing agent and leads to significantly shortened reaction times.

Keywords. Sodium borohydride; Ammonium carbonate; Aldehydes; Ketones; Reduction.

Introduction

Most reductions of carbonyl and other functional groups are now achieved with reagents that transfer a hydride ion from aluminum or boron [1–8]. Sodium borohydride and lithium aluminum hydride are not only the most familiar reagents, but also display a range in selectivity, with sodium borohydride as a mild reducing agent. Several factors affect its reactivity. These include the nature of the metal cation present [9] and the ligands of the complex hydride [10].

In this paper, we wish to report a new system for the reduction of aldehydes and ketones with sodium borohydride in the presence of ammonium carbonate. The present method is mild and effective, uses an inexpensive reagent, needs only rather short reaction times compared with sodium borohydride alone, and thus offers significant advantages.

Results and Discussions

In a typical procedure 1–3 mmol ammonium carbonate and sodium borohydride (see Table 1) are added to the solution of 1 mmol carbonyl compound in 15 cm^3 of

---

[*] Corresponding author. E-mail: mohannazadeh@irost.org

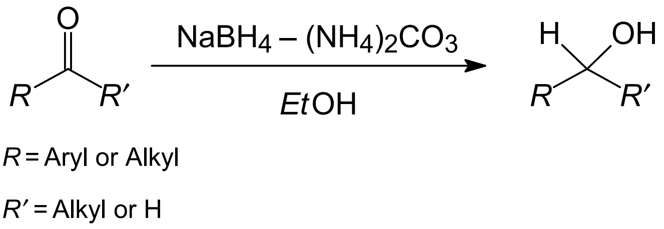
Table 1. Reduction of aldehydes and ketones with the system sodium borohydride – ammonium carbonate

Entry	Educt	Mol ratio			Time[a] min	Yield[b] %
		Educt	$NaBH_4$	$(NH_4)_2CO_3$		
1	benzaldehyde	1	1	1	4	83
2	benzaldehyde	1	1	0	25	80
3	4-bromobenzaldehyde	1	1	1	2	75
4	4-bromobenzaldehyde	1	1	0	17	76
5	4-chlorobenzaldehyde	1	1	1	2	75
6	4-chlorobenzaldehyde	1	1	0	17	75
7	4-dimethylaminobenzaldehyde	1	1	1	5	65
8	4-dimethylaminobenzaldehyde	1	1	0	25	60
9	4-acetylbenzaldehyde[c]	1	1	1	3	78
10	4-methylbenzaldehyde	1	1	1	3	68
11	2-chlorobenzaldehyde	1	1	1	2	76
12	3-hydroxybenzaldehyde	1	1	1	2	72
13	cinnamaldehyde[d]	1	1	1	5	85
14	benzophenone	1	2	2	3	72
15	acetophenone	1	2	2	2	77
16	4-chlorobenzophenone	1	2	2	2	75
17	4-methylacetophenone	1	2	2	4	79
18	benzyl methyl ketone	1	2	2	3	84
19	benzylidine acetone[e]	1	2	2	5	86
20	benzoin	1	2	2	2	80
21	camphor[f]	1	3	3	220	73
22	anthraquinone	1	4	4	40	67

[a] The course of reaction was checked by TLC; [b] isolated pure product; [c] 4-acetylbenzyl alcohol was obtained; [d] cinnamyl alcohol was obtained; [e] 3-hydroxy-1-phenyl-1-butene was obtained; [f] isoborneol was obtained

solvent. The mixture is stirred at room temperature for the time specified in Table 1. The reaction mixture is filtered through a pad of celite and the filtrate is concentrated to give the pure alcohol (Scheme 1).

The rate of reduction increases as the concentration of ammonium carbonate is increased. For example, the reaction time for reduction of 1 eq 4-chlorobenzaldehyde with 1 eq sodium borohydride in the presence of 0, 0.5, and 1 eq ammonium carbonate was 17, 5, and 2 minutes. The same holds for other examples. In all cases a significant shortening of the reaction time was reached.



Scheme 1

Whereas the reaction with aldehydes proceeds readily with only 1 eq sodium borohydride and ammonium carbonate, it is preferable to use 1–4 eq of these reagents in the case of ketones (Table 1). This system also reduces unreactive ketones. A comparison of the results presented in this article with that reported earlier clearly indicates that sodium borohydride – ammonium carbonate is a more effective reagent than sodium borohydride – amberlyst-15 (H^+) [11]. For example, 1 eq camphor is reduced by 40 eq sodium borohydride in presence of amberlyst whereas 3 eq sodium borohydride reduce 1 eq camphor in presence of 3 eq ammonium carbonate. It should be mentioned that reduction of camphor produces the *exo* isomer only.

This method is also very effective for the reduction of aldehyde and ketone functionalities without interfering with sensitive groups, such as chloro, bromo, conjugated double bond, methoxy, and amino, present in the same molecule. Selective reduction of aldehyde in the presence of ketone was demonstrated by conversion of 4-acetylbenzaldehyde to 4-acetylbenzyl alcohol (Table 1).

Experimental

^{1}H NMR spectra were recorded on a *Varian* EM 360A NMR spectrometer using *TMS* as internal standard. IR spectra were taken on a *Perkin-Elmer* 267 spectrophotometer. Thin layer chromatography was performed on silica gel (Machery Nagel Co, Plygram Sil G/uv). Comparison of spectral data (IR, ^{1}H NMR, ^{13}C NMR) and thin layer chromatography with authentic samples confirmed structure and purity of the reported products.

Conversion of Benzaldehyde to Benzyl Alcohol, Typical Procedure

In a round bottomed 50 cm^3 flask equipped with a condenser and magnetic stirrer, a mixture of 0.106 g benzaldehyde (1 mmol) in 15 cm^3 ethanol was prepared. Sodium borohydride (0.038 g, 1 mmol) and 0.096 g $(NH_4)_2CO_3$ (1 mmol) were added to this solution. The mixture was stirred at room temperature for 4 min. Reaction progress was monitored by TLC. After completion of the reaction the mixture was filtered through a pad of celite and the filtrate concentrated under reduced pressure to give the pure product.

References

[1] Brown HC, Rao BC (1956) J Am Chem Soc **78**: 2582
[2] Brown HC, Krishnaurthy S (1973) J Am Chem Soc **95**: 1669
[3] Nose A, Kudo T (1987) Chem Pharm Bull **35**: 1770
[4] Fringuelli F, Pizzo F, Vaccaro L (2000) Synthesis 646
[5] Zanka A, Ohmori H, Okamoto T (1999) Syn Lett **10**: 1636
[6] McGeary RP (1998) Tetrahedron Lett **39**: 3319
[7] Varma RS, Saini R (1997) Tetrahedron Lett **38**: 4337
[8] Masuda R, Inoue T, Izumi T (1982) Tetrahedron Lett **23**: 4585
[9] Ranu BC (1993) Synlett 885
[10] Raber DJ, Guida WC (1976) J Org Chem **41**: 690
[11] Caycho JR, Tellado FG, Armas P (1997) Tetrahedron Lett **38**: 277