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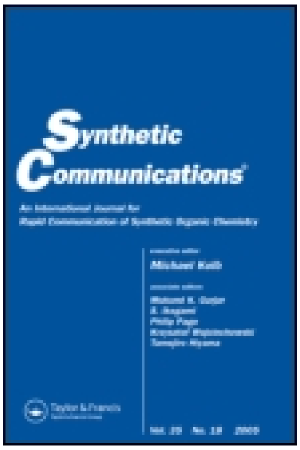

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RAPID REDUCTION OF CARBONYLS WITH NICKEL BORIDE AT AMBIENT TEMPERATURE[1]

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ABSTRACT

Carbonyl compounds have been reported to undergo rapid reduction with nickel boride generated *in situ* from anhyd. nickel chloride and sodium borohydride in THF at ambient temperature to the corresponding alcohols in high yields.

Reduction of carbonyl groups to the corresponding alcohols is one of the important functional group interconversions in organic synthesis. Various reagents have been employed to achieve this transformation namely sodium in ethanol,[2] borane,[3] isopropanol-aluminium triisopropoxide,[4] hydride transfer reagents e.g., lithium aluminium hydride and sodium borohydride,[5] hydrogenation in presence of a suitable catalyst[6] etc. Nickel boride has been reported as a useful catalyst in a number of hydrogenation reactions and offers certain advantages over conventional catalysts.[7] It has also been reported as a catalyst in the hydrogenation of aldehydes to alcohols.[8] Recently it has been reported that nickel boride acts as a reducing

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agent by itself in the absence of hydrogen too.[9] Borbaruah *et al.*[10] have reported that aldehydes can be reduced with nickel boride only in presence of chlorotrimethylsilane. Since nickel boride behaves differently under different reaction conditions, we believed that it may be possible to reduce the carbonyl compounds rapidly with nickel boride under appropriate conditions.

We report herein a simple, rapid and convenient procedure for the reduction of a variety of aldehydes and ketones with nickel boride in tetrahydrofuran at ambient temperature to the corresponding alcohols (eq. 1).

$$\mathrm{RCOR'} \xrightarrow[\text{Dry THF, r.t., }\sim 5\text{–}15\,\text{min}]{\text{Anhyd.NiCl}_2\text{, NaBH}_4} \begin{array}{l}\mathrm{RCHOHR'}\\ \text{High yields}\end{array} \qquad (1)$$

$$\mathrm{R} = \text{Aryl, Alkyl, } \mathrm{R'} = \text{H, Alkyl; R, R'} = \text{Cyclic}$$

The nickel boride was generated *in situ* from anhyd. nickel chloride and sodium borohydride. The reductions were complete in 5–15 min using 1 : 3 : 9 molar ratio of substrate to nickel chloride to sodium borohydride. Longer reaction times were required for complete reduction if lower molar ratios of substrate to $NiCl_2$ to $NaBH_4$ were used, e.g., reduction of benzophenone was complete after 15, 75 and 150 min using 1 : 3 : 9, 1 : 2 : 6 and 1 : 1 : 3 molar ratios respectively (runs 1–3). The alcohols were obtained in nearly quantitative yields by a simple work up. Reductions were also attempted in DMF, CH_3CN and dioxane but THF has been found to be the solvent of choice. The observed reductions are due to the involvement of nickel boride formed *in situ* since benzophenone, veratraldehyde, acetophenone, fluorenone and 4-heptanone did not undergo complete reduction with sodium borohydride only in THF even after 10, 2, 8, 8 and 48 h respectively (runs 4, 6, 8, 10, 27).

The reductions are chemoselective as bromo, chloro, carboethoxy, nitro, isolated double bond and methoxy groups were unaffected under these conditions. The detailed results are presented in Table 1. Nickel boride loses its activity to reduce carbonyl compounds with time. Thus, benzophenone showed complete reduction when added to preformed nickel boride after 15 min but the reduction was incomplete even after 6 h when benzophenone was added to preformed nickel boride after 72 h. The reduction of *N*, *N*-dimethylaminobenzaldehyde and *p*-aminoacetophenone was very sluggish and showed a mixture of products probably because basic nitrogen has been reported to poison the reagent.[11] Reduction of 9-anthrone and xanthone also was not complete even after 240 min and yielded anthracene and xanthene, respectively as the predominant products in these reactions. Anthracene and xanthene are believed to be obtained from the reaction of the initially formed alcohols. This has been confirmed by an

Table 1. Reduction of Carbonyl Compounds with Nickel Boride in Dry THF[a] at Ambient Temperature

Run no.	Substrate RCOR′	Substrate : $NiCl_2$: $NaBH_4$	Time (min)	% Yield RCHOHR′
1	Benzophenone	1 : 3 : 9	15	88[b]
2	Benzophenone	1 : 2 : 6	75	87[b]
3	Benzophenone	1 : 1 : 3	150	82[b]
4	Benzophenone	1 : 0 : 9	600[c]	–
5	Veratraldehyde	1 : 3 : 9	5	87
6	Veratraldehyde	1 : 0 : 9	120[c]	–
7	Acetophenone	1 : 3 : 9	5	86
8	Acetophenone	1 : 0 : 9	480[c]	–
9	Fluorenone	1 : 3 : 9	5	81[d]
10	Fluorenone	1 : 0 : 9	480[c]	–
11	*p*-Chlorobenzaldehyde	1 : 3 : 9	5	84
12	2,4-Dichlorobenzaldehyde	1 : 3 : 9	5	81
13	Benzaldehyde	1 : 3 : 9	5	88
14	*m*-Bromobenzaldehyde	1 : 3 : 9	5	87
15	*p*-Anisaldehyde	1 : 3 : 9	5	85
16	*p*-Tolualdehyde	1 : 3 : 9	5	85
17	Piperonal	1 : 3 : 9	5	86
18	*p*-Nitrobenzaldehyde	1 : 3 : 9	5	65[e]
19	1-Naphthaldehyde	1 : 3 : 9	15	83
20	Butyrophenone	1 : 3 : 9	15	89
21	4,4′-Dichlorobenzophenone	1 : 3 : 9	60	85
22	2-Amino, 5-chlorobenzophenone	1 : 3 : 9	60	85
23	Anthrone	1 : 3 : 9	240	69[f]
24	Xanthone	1 : 3 : 9	240	32[g]
25	Heptaldehyde	1 : 3 : 9	5	90
26	4-Heptanone	1 : 3 : 9	5	92
27	4-Heptanone	1 : 0 : 9	–[h]	–
28	Cyclohexanone	1 : 3 : 9	15	92
29	Cyclopentanone	1 : 3 : 9	5	79
30	2-octanone	1 : 3 : 9	5	86
31	*n*-Hexadecanal	1 : 3 : 9	10	92
32	Δ^5-Cholesten-3-one	1 : 3 : 9	10	80

[a] 25 mL of THF/g of substrate was used.

[b] Benzopinacol (3–4%) was also isolated by column chromatography.

[c] Reduction was incomplete and consisted of a mixture of alcohol and the substrate.

[d] ~2% of fluorene and ~2% of starting material were also recovered by column chromatography.

[e] Reaction mixture didn't turn black on addition of $NaBH_4$ to mixture of reactant and $NiCl_2$ in THF unlike all other reactions and some other products were also formed believed to be the reduction products of the nitro group.

[f] Reaction was incomplete even after 4 h and the product isolated was anthracene.

[g] Reaction was incomplete even after 4 h and product isolated was xanthene; rest of the mixture consisted of xanthone and xanthydrol.

[h] Reaction was incomplete even after 2 days.

independent reaction of xanthydrol with nickel boride which yielded xanthene under identical reaction conditions.

EXPERIMENTAL

All the commercial carbonyl compounds were used after distillation/recrystallization. THF was dried by reported procedure.[12] Sodium borohydride (E. Merck) and anhyd. Nickel chloride (Qualigens) were used in all the reactions. Products were analyzed by m.p., mixed m.p. (wherever applicable), IR and NMR spectra.

In a typical experiment, carbonyl compound (1 g, n mmol), dry THF (25 mL) and anhyd. $NiCl_2$ (3n mmol) were placed in a 100 mL round-bottomed flask fitted with a reflux condenser, a $CaCl_2$ guard tube and mounted over a magnetic stirrer. $NaBH_4$ (9n mmol) was added and formation of black precipitate of nickel boride was observed immediately. The reaction mixture was stirred at room temperature and its progress was monitored by TLC for disappearance of starting material. The reaction mixture was diluted with dichloromethane (~ 75 mL) and filtered through a celite pad. The filtrate was diluted with water (~ 100 mL) and extracted with dichloromethane (3 × 10 mL). The combined dichloromethane layer was dried (anhyd. $MgSO_4$) and concentrated on a Buchi rotavapor to give the alcohol which was recrystallized or purified by column chromatography over silica gel (100–200 mesh) using petroleum ether and/or benzene as eluent. In case of aliphatic alcohols, the combined filtrate was concentrated on a rotary evaporator and the resulting residue was dissolved in anhyd. diethyl ether. The ether layer was filtered and the filtrate dried over anhyd. $MgSO_4$. The filtrate was concentrated on a rotary evaporator and yielded the alcohol.

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