

Nickel-mediated hydroboration reactions

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Abstract. Reactivity of sodium borohydride with olefins in the presence of NiL_nCl_2 (where $\text{L} = 2,2$ bipyridyl, pyridine, triphenyl phosphine) has been studied. Hydrogenation as well as hydroboration on olefins is observed. Nitrogen donor ligands favour hydroboration on olefins when a nickel borohydride system is used.

Keywords. Nickel complexes; sodium borohydride; hydroboration; hydrogenation.

1. Introduction

Functional groups like amides and nitro groups can be reduced by transition metal borohydride systems (Sceifels *et al* 1981). Complete exploitation of these reactions is yet to be made (Hanya *et al* 1979; Heinzmann and Ganem 1982). Periasamy and his co-workers (Satyanarayana and Periasamy 1984, 1986, 1987; Achyutha Rao and Periasamy 1986) and Cowan (1986) have demonstrated that the metal borohydride systems can hydroborate as well as hydrogenate olefins and their reactivities are influenced by the metal ion as well as by attached ligands. The nickel borohydride system was successfully used by Brown and Brown (1963) for hydrogenation of olefins, however, the capability of the nickel borohydride system for hydroboration has not been studied. In this report, we demonstrate that the reactivity of the nickel borohydride system is greatly influenced by the solvent and the ligand used, and hydroboration can be achieved under appropriate conditions.

2. Experimental

Dichloro *bis*-triphenyl phosphine nickel(II) (Chatt and Shaw 1960) and dichloro mono bipyridyl nickel(II) (Uchino *et al* 1975) were prepared by the literature procedures.

2.1 Conversion of olefins to alcohols

To a well-stirred acetonitrile solution of olefin (8 mmol) and $\text{Ni}(\text{Bpy})\text{Cl}_2$ (8 mmol) (where Bpy = bipyridyl), sodium borohydride (10 mmol) was added in small portions. An exothermic reaction took place and the reaction mixture was stirred at room

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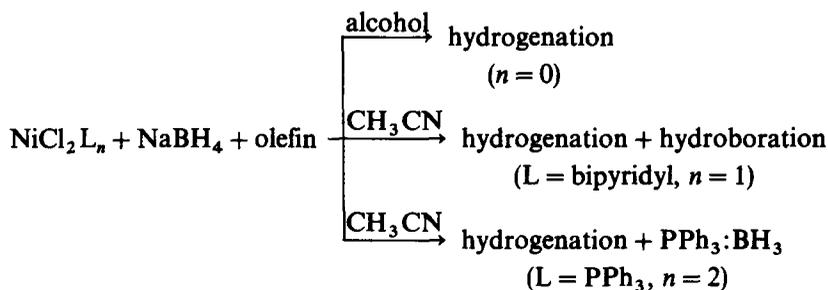
temperature for 8 h. The reaction mixture was worked up following the method described in the literature (Brown and Subba Rao 1956) to obtain the corresponding alcohol and hydrocarbon. The products were further characterised after purification by recording their $^1\text{H NMR}$ and IR spectra and comparing them with those of authentic samples.

2.2 Preparation of borane triphenyl phosphine

To a well-stirred solution of $\text{NiCl}_2(\text{PPh}_3)_2$ (590 mg, 1 mmol), sodium borohydride (39 mg, 1 mmol) was added in small portions. The reaction mixture was stirred at 25°C for half an hour, and the acetonitrile then removed under reduced pressure. The crude mixture was taken on a silica gel column and eluted with petroleum ether to obtain the borane triphenyl phosphine complex (225 mg, 86%) m.p. 181°C (reported $182\text{--}186^\circ\text{C}$, Das and Roy 1985). $^1\text{H NMR}$ (CDCl_3): 7.5 (m, 15 H) 1.56 (br q, 1:1:1:1, $J = 80\text{ Hz}$, 3 H), IR (nujol): 2830, 2340 cm^{-1} .

3. Results and discussion

Nickel (II) acetate, along with sodium, borohydride hydrogenates olefins in protic media (Brown and Brown 1963), but is not suitable for the hydroboration reaction. In our present study, we observe that nickel complexes having nitrogen donor ligands are capable of hydroborating olefins in the presence of sodium borohydride (scheme 1). Olefins like styrene, cyclohexene, cyclooctene and 1-octene can be converted to the saturated alcohols.



Scheme 1.

Control experiments were performed to study the effect of the solvent ligand on the reactive species. $\text{NiCl}_2(\text{Bpy})$ was found to be a suitable complex for performing hydroboration. Reaction of styrene with sodium borohydride in the presence of NiCl_2 in acetonitrile medium showed considerable hydroboration along with hydrogenation of styrene. This observation is comparable to the result on the Co/BH_4 system published by Periasamy and his co-workers (Satyanarayana and Periasamy 1984) where they observe remarkable change in reactivity owing to change of solvent from methanol to THF. In order to study the modification of the reactive species by coordination of solvent we have examined the reaction of nitrogen donor ligands. The results are summarised in table 1.

Sodium borohydride reacts with $\text{NiCl}_2(\text{PPh}_3)_2$ and results in the formation of a $\text{PPh}_3\text{:BH}_3$ complex; however, this system fails to hydroborate olefin at room

Table 1. Comparative results on preferences of hydroboration over hydrogenation.

Olefin	Nickel complex	Solvent	Ratio ^a of hydrogenation: hydroboration
Styrene	Nickel acetate	Alcohol	100:0 ^b
Styrene	NiCl ₂	Alcohol	100:0
Styrene	Ni(BPY)Cl ₂	Alcohol	30:70
Styrene	Ni(BPY)Cl ₂	Acetonitrile	0:100
Styrene	NiCl ₂	Acetonitrile	50:50
Styrene	NiCl ₂	Acetonitrile/ pyridine	30:70
Cyclohexene	Ni(BPY)Cl ₂	Acetonitrile	0:100
Cyclooctene	Ni(BPY)Cl ₂	Acetonitrile	0:100

^a From ¹H NMR, ^b from the work of Brown and Brown (1963).

temperature. This system can act as a hydrogenating reagent. For example, styrene forms ethyl benzene on reaction with NaBH₄ in the presence of NiCl₂(PPh₃)₂. The isolation of PPh₃:BH₃ suggests that hydroboration proceeds via *in situ* generation of BH₃ as the reactive species. The presence of nitrogen donor ligand may have two-fold effects, viz. to react with BH₃ to stabilise it from further reaction with the metal ion, and to stabilise the higher oxidation state. PPh₃:BH₃ being the less reactive complex fails to hydroborate olefin.

The results presented suggest that the Ni²⁺/BH₄ system can be modified to hydroborate olefins and its reactivity is comparable to that of other transition metal-borohydride systems.

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