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Reduction of α,β unsaturated carbonyl compounds by $Ni^{2+}-BH_4^-$

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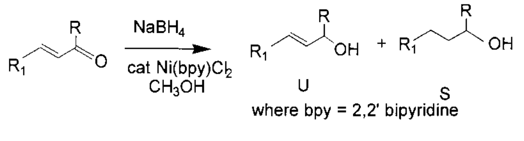
Abstract

The reduction of α,β unsaturated carbonyl compounds by sodiumborohydride is catalysed by $Ni(bpy)Cl_2$ (bpy = 2,2′-bipyridine). Various carbonyl compounds having the general formula $R_1CH{=}CHCRO$ [where R_1, R = C_6H_5, H; *p*-MeO–C_6H_4–,C_6H_4; *p*-CH_3–C_6H_4, C_6H_5; (*m*-OMe–)(*p*-OMe–)C_6H_3, C_6H_5; C_6H_5, $(CH_3)_2CH$–; CH_3, H; *m*-Br–C_6H_4–, C_6H_5] are reduced to corresponding allylicalcohol [$R_1CH{=}CHCRHOH$] at 25°C within half an hour. During these reductions the double bond is partially reduced to give saturated alcohols as minor products having the molecular formula $R_1CH_2CH_2CRHOH$. The reduction of *trans*-3-phenyl-2-propenal with $NaBH_4$ and catalytic amounts of $Ni(bpy)Cl_2$ in solvents containing active deuterium (D_2O, CD_3OD), leads to the partial incorporation of deuterium at the α and γ positions to give C–D bonded alcohols. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Sodiumborohydride; Nickel catalyst; Reduction; Deuteration; α,β Unsaturated carbonyl compounds

1. Introduction

The reduction of organic compounds is a common reaction extensively used in synthetic chemistry and in industry [1]. New reagents are developed for optical induction and selective reduction of unsaturated and carbonyl compounds [2]. The reduction of α,β unsaturated carbonyl compounds has been thoroughly exploited and continues to attract attention [3]. Sodiumborohydride can cause selective reduction of α,β unsaturated carbonyl compounds and sodiumborohydride, and in combination with various metal catalysts can cause hydrogenation and hydroboration of unsaturated compounds [4]. The enhancement of selectivity and efficacy of these reactions continues to be a nodal point to diverse [2]. The reduction of unsaturated compounds can efficiently be carried out by the reaction of hydrated nickel chloride in the presence of radical anions [5a]. However, such reactions require the generation of anion radicals by reactive alkali metals and they require extensive care in handling. The incorporation of deuterium from performed deuterohydrated nickel chloride to unsaturated organic compounds makes these reactions attractive, and exploration of new reagents have increasing demand [5b]. Reports are available on partial incorporation of deuterium on carbonyl compounds by borohydride anions without a catalyst as well as in the presence of late transition metal complexes [6]. This article describes the use of nickel catalysts to modify the course of the reduction reaction of α,β unsaturated carbonyl compounds by sodiumborohydride under neutral condition, and also on the incorporation of deuterium from solvent-containing active deuterium into the products of such reactions.



Scheme 1.

2. Results and discussion

The reaction of *trans*-3-phenyl-2-propenal with sodium borohydride and a catalytic amount of $Ni(bpy)Cl_2$ (bpy = 2,2′ bipyridine) leads to *trans*-3-

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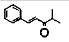
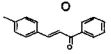
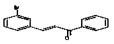
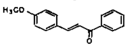
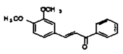
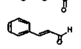
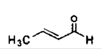
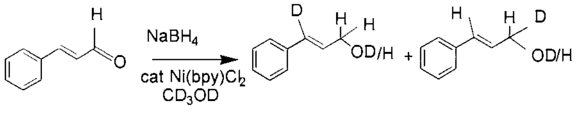
Table 1
Results on Ni(bpy)Cl_2 catalysed reduction

Entry	Substrate	Ratio of U : S (as in scheme 1)	% Conversion to alcohol
1.		36 : 64	98
2.		84 : 16	96
3.		81 :19	90
4.		100:0	98
5.		100:0	100
6.		94 : 6	100
7.		83 : 17	96



Scheme 2.

phenyl-2-propen-1-ol along with 3-phenylpropan-1-ol within 30 min. The reaction is applicable to other α,β unsaturated carbonyl compounds (Scheme 1) and is substrate dependent. The results on product ratios of unsaturated (U) and saturated (S) alcohols are shown in Table 1. The catalytic activity of different nickel salts was tested by comparing their percentage conversion of the reduction of *trans*-3-phenyl-2-propenal after a 15 min time interval of independent experiments and reactivity are in the order of Ni(bpy)Cl_2 > bis-triphenylphosphinenickel(II)chloride > nickel(II)acetate > nickel(II)chloridehexahydrate. The product ratios of saturated and unsaturated (U:S as in Scheme 1) are effected by the nickel catalyst and in each case the saturated (S) and unsaturated products were formed in approximately equal ratios except in the case of Ni(bpy)Cl_2. In this case, the maximum selectivity on the formation of unsaturated alcohol was observed (> 90%).

The significant feature of these reactions is the transfer of active deuterium from the solvent containing active deuterium during reduction to form C–D bond. It was observed that the reaction of *trans*-3-phenyl-2-propenal in deuteriumoxide with Ni(bpy)Cl_2 as the catalyst gave *trans*-3-phenyl-2-propen-1-ol with the incorporation of deuterium at α and γ positions in a 43:57 ratio. Deuterium incorporation from D_2O does not occur without the use of the nickel catalyst (Scheme 2). A similar observation was also observed from the reaction of sodiumborohydride in methanol-d_4. The reaction of *trans*-3-phenyl-2-propenal with sodiumborohydride in the presence of Ni(bpy)Cl_2 catalyst has yielded the deuterated saturated and unsaturated alcohols. Fig. 1(a) and (b) show the NMR spectra of the reaction mixture in which the reduction of *trans*-3-phenyl-2-propenal with sodium borohydride carried out in methanol-d_4 with and without Ni(bpy)Cl_2. The multiplicity of α and γ protons in ^{1}H-NMR clearly discerns the incorporation of deuterium at these positions when the Ni(bpy)Cl_2 was used as a catalyst. In the undeuterated *trans*-3-phenyl-2-propen-1-ol the α and γ protons appear at δ 6.56 as a doublet ($J = 18$ Hz, *trans* coupling) and at δ 6.34 as a doublet of a triplet (18 and 9 Hz, respectively). However, the product obtained from the reaction in CD_3OD by the Ni^{2+}–BH_4^- system and the coupling pattern of the signal at δ 6.56 is not affected but becomes slightly broadened due to the presence of deuterium with $I = 1$ and the signal at δ 6.34 appears as a multiplet due to the presence of deuterium at the α and γ positions. The integrations confirm the ratio of deuterium at the α and γ position as 46:54. The proton signal at δ 4.21 appearing as a doublet of a multiplet ($J = 9$ Hz) from saturated carbon (γ position) also indicates the deuterium being incorporated at the γ position. Only the *trans* unsaturated alcohol was obtained in these reactions. About 7% 3-phenyl propan-1-ol was also obtained on reduction by the Ni^{2+}–BH_4^- system.

A plausible path leading to the incorporation of deuterium during the reduction of the α,β unsaturated carbonyl compound is shown in Scheme 3. The generation of reduced nickel(0) complexes similar to (**A**) (Scheme 3) by reducing agents is established [7]. A methanolic solution of Ni(bpy)Cl_2 has its absorption maximum at 296 and 306 nm due to the metal to ligand charge transfer [11]. These absorptions disappear after the addition of sodium borohydride (Fig. 2) and a new absorption at 282 nm develops. Vigorous hydrogen gas evolution occurs initially and once the borohydride is consumed, the two absorption maxima at 296 and 306 nm reappear and the absorption at 282 nm disappears. This suggests that an intermediate [7c] of Ni(0) of the type (**A**) having absorption at 282 nm gets converted to Ni(II) species during the dehydrogenative coupling reaction [7]. A similar pattern on the change of absorbance was also observed during the reduction reaction of *trans*-3-phenyl-2-propenal by sodiumborohydride in the presence of Ni(bpy)Cl_2 in methanol. An oxidative addition and reductive elimination process may be favourable to explain the equi-distribution of deuterium at the α and γ positions. Since the exchange of deuterium at α and γ positions were approximately equal, it suggests intermediacy of the π-allylic type of complex in the reaction. There are several structural possibilities of such intermediates and in view of the inability to isolate such intermediates the discussion is minimised. The existing literature suggests that the

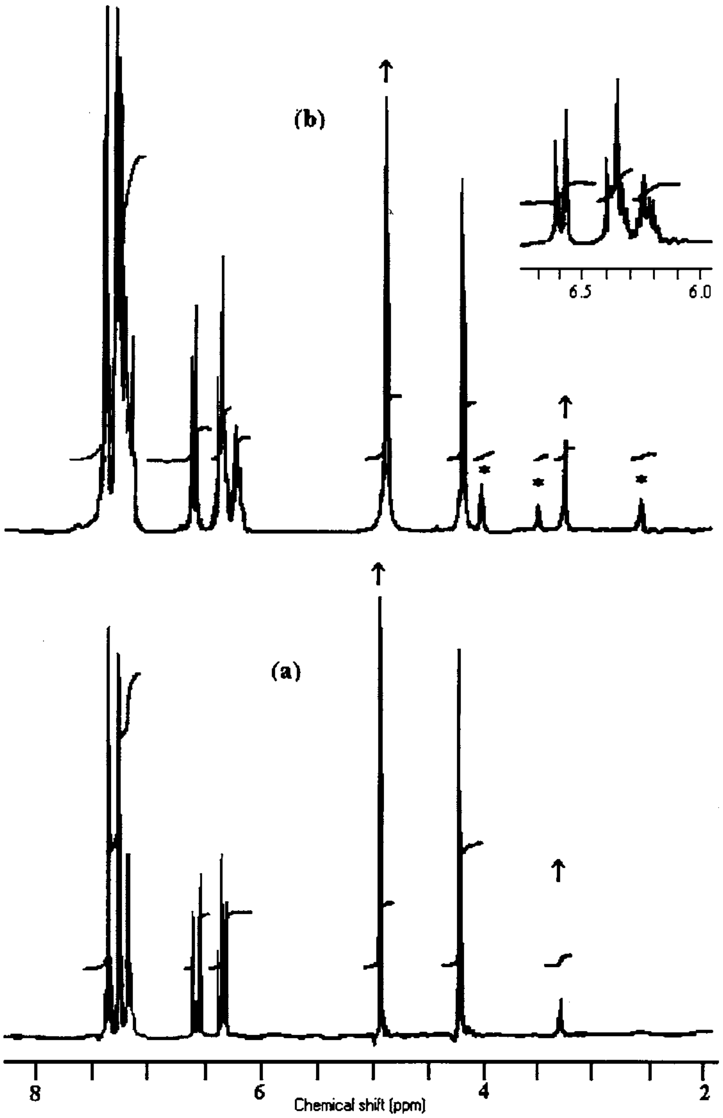
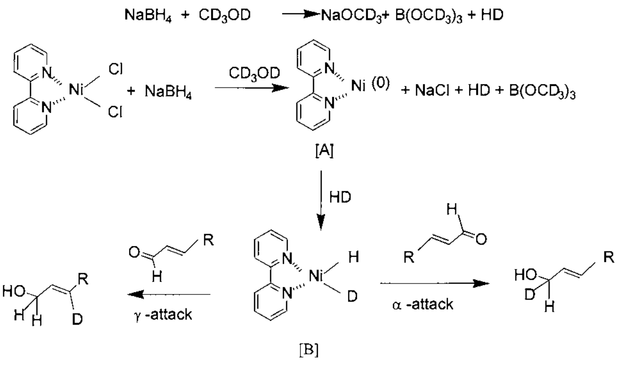


Fig. 1. The 400 MHz ^{1}H-NMR of the reaction mixture of *trans*-3-phenyl-2-propenal with sodium borohydride in CD_3OD (a) without Ni (bpy)Cl_2 catalyst; (b) with Ni (bpy)Cl_2 catalyst (* are signals from the saturated alcohol and ↑ are from the solvent). Inset is the expansion of α and β-proton signals of (b).

carbonyl compounds can be partially deuterated by sodium borohydride [6a] and the partial deuteration of the carbonyl compound by sodiumborohydride in deuterated solvents is enhanced by heavy metal salts such as that of platinum [6b]. However, our reactions are performed under neutral conditions and the selective carbonyl reductions of α β unsaturated carbonyl compounds are observed. The dehydrogenative coupling reactions by other hydrides such as deuterosilanes in the presence of transition metal catalysts also allows hydrogenation of olefins through deuterium scrambling on the products [8].

In conclusion this study showed the catalytic effect of Ni(bpy)Cl_2 during the sodiumborohydride reduction and also has shown that the deuterium can be partially incorporated from a deuterated solvent containing active deuterium to an α,β unsaturated carbonyl compound.



Scheme 3.

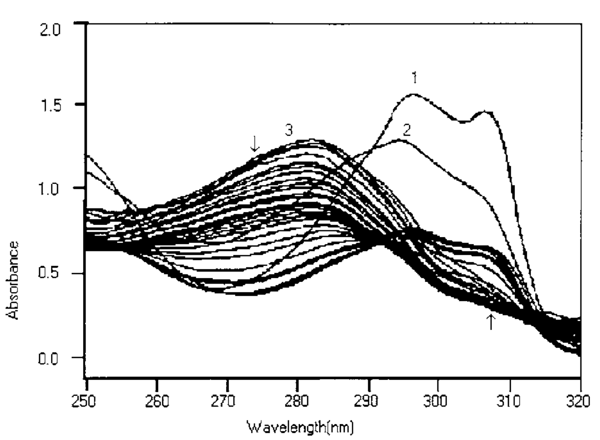
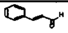
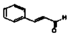
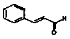
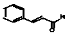


Fig. 2. Change of absorbance spectra of a methanolic solution containing Ni(bpy)Cl_2 (0.023 mmol) with sodium borohydride (0.05 mmol) after 2 min time intervals.

Table 2
Results on deuterium incorporation [a]

Sl No.	Substrate	Ratio of U : S (as in scheme 1)
1		94 : 6
2[b]		100 : 0 (no deuteriumon U)
3[c]		91 : 9 (ratio of α and γ deuterated on U is 43 : 57)
4[d]		93 : 7 (ratio of α and γ deuterated on U is 46 :54)

[a] Unless stated in all cases, the reactions were carried out at r.t. by using α,β unsaturated carbonyl compound (1 mmol), $NaBH_4$ (2 mmol), Ni(bpy)Cl_2 (0.01 mmol) in methanol (2 cm^3) for half an hour. The products were characterised by purification and comparing their 400 MHz ^{1}H-NMR and IR with authentic sample; a, in the absence of Ni(bpy)Cl_2; b, Without Ni(bpy)Cl_2 catalyst in CD_3OD; c, with Ni(bpy)Cl_2 catalyst in D_2O; d, with Ni(bpy)Cl_2 catalyst in CD_3OD.

3. Experimental

The α,β unsaturated carbonyl compounds used in this study were either prepared by standard procedure [9] or obtained from E. Merck and used as procured. The Ni$(PPh_3)_2Cl_2$ [10], Ni(bpy)Cl_2 [11] were prepared by the reported procedure. The deuterium incorporation experiments were monitored by studying the reaction in a NMR tube by mixing appropriate amounts of the reagents in each case (refer to footnote of Table 2).

3.1. The reduction of α,β unsaturated carbonyl compounds

To a well stirred solution containing α,β unsaturated carbonyl compound (1 mmol), Ni(bpy)Cl_2 (0.01 mmol) in methanol (2 cm^3), the $NaBH_4$ (2 mmol) was added in portions. A rapid reaction took place with vigorous gas evolution and the reaction mixture was stirred for 30 min at room temperature (25°C). The solution turned black. To the reaction mixture, CH_2Cl_2 (20 cm^3) was added, followed by the addition of HCl (1% in 5 cm^3 water). The CH_2Cl_2 layer was separated and dried over anhydrous sodium sulphate and filtered. Removal of the solvent under reduced pressure gave the corresponding alcohols in near quantitative yield (refer to Table 1). The products were purified by column chromatography except in the case of the reduced product of crotonaldehyde where purification was done by distillation. The saturated and unsaturated alcohols were obtained as a mixture. The purified alcoholic compounds were characterised by comparing their 400 MHz ^{1}H-NMR and IR with an authentic sample.

Acknowledgements

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