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HYDROBORATION OR HYDROGENATION OF ALKENES WITH $CoCl_2$-$NaBH_4$

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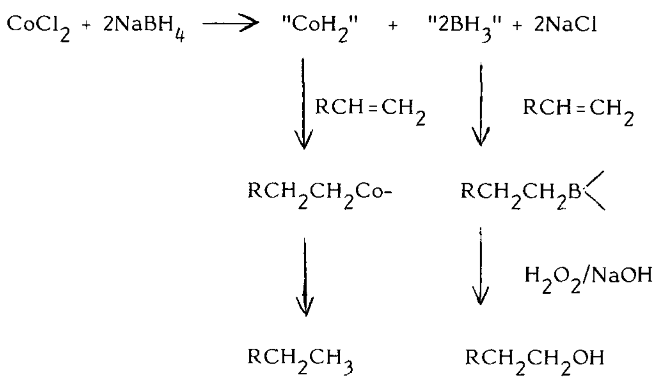
Abstract: The $CoCl_2$-$NaBH_4$ reagent hydroborates or hydrogenates alkenes under appropriate conditions.

Alkenes can be hydrogenated using sodium borohydride in the presence of $CoCl_2.6H_2O$ or $CoCl_2$ in alcoholic medium.[1] It has been suggested that the reaction goes via hydrocobaltation.[1]

$$CoCl_2 + NaBH_4 \longrightarrow LnCoH \xrightarrow{RCH=CH_2} RCH_2CH_2CoLn \longrightarrow RCH_2CH_3$$

In the course of our investigation[2] on the carbonylation of organometallics produced in such a simple manner, we have observed that the mixture of anhydrous $CoCl_2$ and $NaBH_4$ in THF behaves as if it contains "CoH_2" and "BH_3" species. We wish to report that the reaction of $CoCl_2$-$NaBH_4$ reagent with alkenes can be directed to give either hydroboration or hydrogenation.

It has been reported that the reduction of alkenes using $CoCl_2.6H_2O$-$NaBH_4$ reagent is sluggish in anhydrous tetrahydrofuran (THF).[1] However, we have observed that upon addition of $NaBH_4$ (20 mmol) into a mixture of 1-decene (20 mmol) and anhydrous $CoCl_2$ (10 mmol) in THF (40 ml) under N_2 at 0°C for 1 h, no 1-decene remained unreacted. The reaction mixture was treated with 3N HCl and worked up as reported.[1] Decane was isolated in 40-50% yield. However, lot of less volatile residue was left behind in the distillation flask. Oxidation of this residue with H_2O_2/NaOH gave 1-decanol. This observation suggests that the residue may be organoboron species. Presumably, the reaction of $CoCl_2$ with $NaBH_4$ in THF gives species which could hydroborate or hydrocobaltate alkenes.



If this is the case it should be possible to direct the reaction to give the hydroboration product by preventing hydrocobaltation. Also, it should be possible to achieve hydrocobaltation by preventing hydroboration. We have found that these objectives can be achieved by simple manipulation of the experimental conditions.

When the $CoCl_2$-$NaBH_4$ mixture in THF was stirred for 2 h at room temperature before the addition of alkene, the reagent behaves as a hydroborating agent. Presumably, the cobalt hydride species gets destroyed by the formation of cobalt metal[3] or cobalt boride species.[4] The following is the typical procedure for hydroboration-oxidation.

Sodium borohydride (20 mmol) was added in portions into $CoCl_2$ (10 mmol) in THF (40 ml) under nitrogen at 0°C for 1 h and the mixture was stirred further for 2 h at room temperature. 1-Decene (40 mmol) was added and the mixture was stirred for 3 h at room temperature. The reaction mixture was added to 3N HCl and the THF layer was separated after saturating with NaCl.[5] The contents of the THF solution was oxidised with H_2O_2/NaOH following the usual procedure for the oxidation of organoboranes.[6] 1-Decanol was isolated in 70% yield. The reaction is found to be a general one (Table 1). The regio- and stereospecificities are similar to the reactions with other borane reagents.[6]

It is apparent that if we could devise a method to prevent hydroboration, we could direct the reaction to achieve hydrocobaltation-reduction.

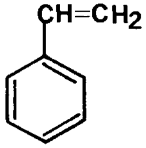
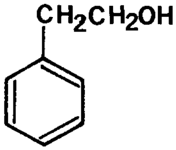
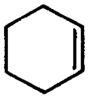
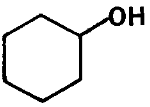
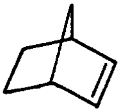
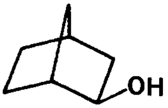
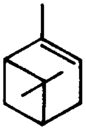
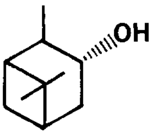
We have observed that addition of $CoCl_2$ (10 mmol) into a mixture of $NaBH_4$ (20 mmol) and methanol (60 mmol) in THF under nitrogen for 1 h at 0°C followed by addition of alkene (20 mmol) and further stirring the reaction mixture as outlined in Table 2 gives alkanes in good yields. The hydrogenated products were isolated by treating the reaction mixture with 3N HCl followed by work up similar to the reported procedure.[1]

The terminal and disubstituted alkenes do not pose any problem (Table 2). However, trisubstituted olefins (eg. α-pinene and cholesterol) do not undergo hydrogenation. However, this method works out favourably for the selective hydrogenation of the disubstituted terminal double bond in the presence of the trisubstituted double bond as observed in the case of the reduction of limonene (Table 2).

The present method has some advantages over the reported method using alcoholic medium.[1] The new method utilises 2 moles of alkene per mole of $CoCl_2$ whereas the reported procedure[1] utilises only one mole of alkene per mole of $CoCl_2$. More importantly, the present method utilises an aprotic solvent which should be a better medium for intercepting the organocobalt species.

We are now actively investigating the synthetic possibilities of the organometallic species produced in such simple reactions.

Table 1 : Hydroboration of Alkenes with $CoCl_2/NaBH_4$[a]

Alkene	Product[b]	Yield [%][c]
$CH_3(CH_2)_7CH=CH_2$	$CH_3(CH_2)_7CH_2CH_2OH$	70
		68[d]
		85
		90
		70

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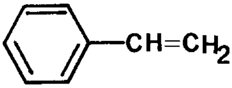
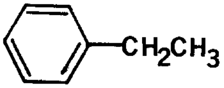
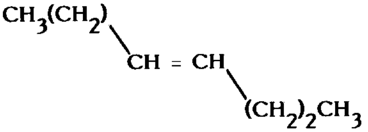
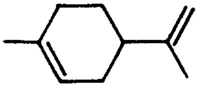
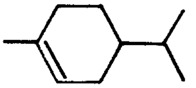
[a] The reactions were carried out using 40 mmol of alkenes, 20 mmol of $NaBH_4$ and 10 mmol of $CoCl_2$ in THF (40 ml) under nitrogen atmosphere. THF used was distilled over benzophenone-sodium. Cobalt(II) chloride supplied by Alfa-USA and the sample prepared by the dehydration of $CoCl_2.6H_2O$ using 2,2-dimethoxypropane work equally well. Sodium borohydride supplied by Fluka-Switzerland and the sample supplied by Loba-Cheme-India give identical results.

[b] Products obtained after oxidation with $H_2O_2/NaOH$. The products were identified by spectral data (i.r., ^1H-NMR and ^{13}C-NMR) and comparison with the data reported in the literature.

[c] Yields are of the isolated and distilled products.

[d] The isomeric 1-phenylethanol is present to the extent of 18%. Products in other cases contain only small amount of the isomeric alcohols ($<5\%$).

Table 2: Hydrogenation of Alkenes with $NaBH_4/CH_3OH-CoCl_2$ in THF[a]

Alkene	Reaction time [h][b]	Product[c]	Yield[d] [%]
$CH_3(CH_2)_7CH=CH_2$	3	$CH_3(CH_2)_7CH_2CH_3$	80
	3		65
 $CH_3(CH_2)CH=CH(CH_2)_2CH_3$	8	$CH_3(CH_2)_6CH_3$	70
α-Pinene	12	No reaction	
Cholesterol	12	No reaction	
	8		75

[a]The reactions were carried out using 10 mmol of $CoCl_2$, 20 mmol of $NaBH_4$, 60 mmol of CH_3OH and 20 mmol of alkene in THF (40 ml).

[b]Time taken after the addition of the alkene into the mixture containing $NaBH_4$-CH_3OH-$CoCl_2$ in THF.

[c]The products were identified by spectral data (i.r., ^1H-NMR and ^{13}C-NMR) and comparison with the data reported in the literature.

[d]Yields are of the isolated and distilled products.

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References

1. S.K. Chung, J. Org. Chem., 1979, 44, 1014.
2. C. Narayana and M. Periasamy, Synthesis, a review manuscript submitted for publication.
3. In alcoholic medium, $CoCl_2$ has been reported to react with $NaBH_4$ to produce Co metal, $Co(BH_4)_2$ and complexed cobalt hydrides (R.A. Shunn in "Transition metal hydrides", Vol.1, E.L. Muetterties, Ed., Marcel Dekker, New York, 1971, p.203).
4. H.I. Schlesinger, H.C. Brown, A.E. Finholt, J.R. Gilbreath, H.R. Hoekstrer and E.K. Hyde, J. Am. Chem. Soc., 1953, 73, 215.
5. This operation is necessary because oxidation by direct addition of H_2O_2/OH^- is violent.
6. H.C. Brown, Organic Synthesis via Boranes, Wiley-Interscience, New York, 1975.

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