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# Ruthenium catalysed reduction of alkenes using sodium borohydride

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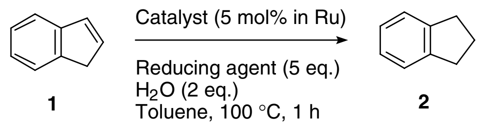
**Abstract**—The reduction of alkenes has been achieved using $NaBH_4$ as the reducing agent using 0.5–1.0 mol % $Ru(PPh_3)_4H_2$ in the presence of water.

The transition metal catalysed reduction of alkenes is generally acheived using hydrogen gas or by transfer hydrogenation from a suitable hydrogen donor. Amongst the various transition metals that are able to catalyse the reduction of alkenes, homogeneous ruthenium complexes play a significant role.[1] We have recently been interested in the use of ruthenium complexes in oxidation and reduction processes, and wanted to identify alternative reducing agents for alkenes.[2] Herein, we report the ruthenium catalysed reduction of alkenes using sodium borohydride. Sodium borohydride is normally associated with the reduction of polar functional groups, such as carbonyl compounds. However, it is known that in the presence of simple metal salts, sodium borohydride can be used to reduce a wider range of functionality, including alkenes.[3] Transition metals have also been shown to catalyse the generation of hydrogen from sodium borohydride.[4]

Preliminary experiments were performed with 5 mol % of a ruthenium catalyst using an excess reducing agent in order to convert indene **1** into indane **2** (Scheme 1, Table 1).



**Scheme 1.** Ruthenium catalysed reduction of indene.

**Table 1.** Study of ruthenium catalysts for the reduction of indene **1**

| Catalyst (5 mol % in Ru) | Reducing agent (4 equiv) | Conversion (%)[a] |
|---|---|---|
| $CpRuCl(PPh_3)_2$ | $NaBH_4$ | 0 |
| $CpRuCl(PPh_3)_2$/KOH | $NaBH_4$ | 100 |
| $[(p\text{-cymene})RuCl_2]_2$ | $NaBH_4$ | 97 |
| $[(p\text{-cymene})RuCl_2]_2$/KOH | $NaBH_4$ | 100 |
| $PhCH=Ru(PCy_3)_2Cl_2$ | $NaBH_4$ | 90 |
| $Ru(PPh_3)_3CO(H)_2$ | $NaBH_4$ | 100 |
| $Ru(PPh_3)_3CO(H)_2$ | $NaBH_4$ | 31[b] |
| $Ru(PPh_3)_3CO(H)_2$ | $Bu_3N{\cdot}BH_3$ | 100 |
| $Ru(PPh_3)_4(H)_2$ | $C_5H_5N{\cdot}BH_3$ | 100 |
| $Ru(PPh_3)_4(H)_2$ | $H_3N{\cdot}BH_3$ | 77 |
| $Ru(PPh_3)_4(H)_2$ | $NaBH_4$ | 100 |
| None | $NaBH_4$ | 0 |

[a] Conversion was determined from analysis of the $^1H$ NMR spectra.
[b] No water added.

Alternative proton sources including ammonium chloride, pyridinium *p*-toluenesulphonate and carboxylic acids were less successful, in the latter cases leading to the reduction of the carboxylic acid into an alcohol under the reaction conditions.

Optimisation experiments led to the use of significantly reduced catalyst loading (down to 0.5 mol %) for the reduction of indene **1** and stilbene **3**. However, some other substrates gave either incomplete reduction or by-products under these conditions. For example, the reduction of *p*-allylanisole **4** afforded the reduction product **6a** along with the isomerised product **6b** (Scheme 2).

In subsequent reductions, we used 1 mol % catalyst for 22 h, in order to ensure a complete reduction. Using

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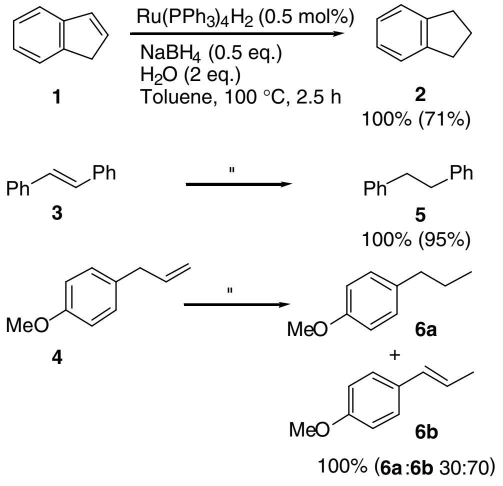
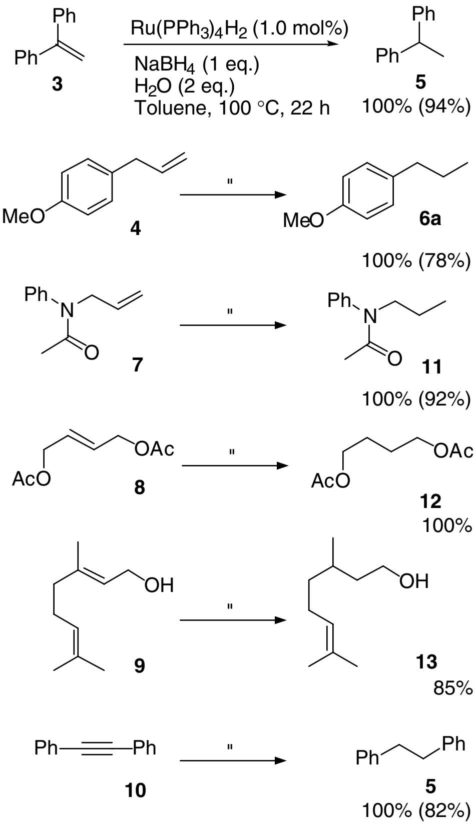


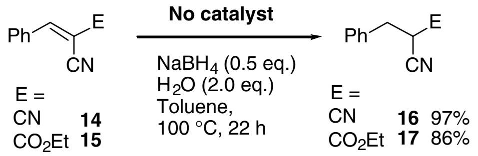
**Scheme 2.** Reduction (and isomerisation) of alkenes. Conversions, with isolated yields in parentheses.



**Scheme 3.** Reduction of other alkenes.

these conditions, a range of alkenes was reduced (Scheme 3).

The longer reaction times allowed alkene **4** to be reduced without any isomerisation product remaining. Amide and ester functionalities in substrates **7** and **8** were tolerated. Geraniol **9** was reduced selectively at the allylic position,[5] and alkyne **10** was also fully reduced to the alkane. The more highly substituted alkenes triphenylethene and tetraphenylethene were found to be essentially inert to reduction under these conditions.



**Scheme 4.** Uncatalysed reduction of electron deficient alkenes.

Control experiments demonstrated that no reduction of the alkenes in Scheme 3 was observed in the absence of a catalyst. However, the electron deficient alkenes **14** and **15** were readily reduced without a catalyst (Scheme 4).

Overall the reduction procedure allows hydrogenation reactions to take place without the need for an external supply of hydrogen.[6] We assume that the ruthenium complex catalyses both the formation of hydrogen from borohydride/water and the subsequent reduction process.

In summary, we have shown that ruthenium catalysts are capable of reducing alkenes using sodium borohydride/water as an alternative reducing agent.

## Acknowledgements

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## References and notes

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6. Experimental procedure for the reduction of stilbene: (*E*)-stilbene (450 mg, 2.5 mmol), sodium borohydride (47.5 mg, 1.25 mmol), water (90 mg, 5 mmol) and $Ru(PPh_3)_4H_2$ (14 mg, 0.5 mol %) in toluene (5 mL) were heated at 100 °C for 2.5 h in a pressure tube (*Caution*: hydrogen evolved). After cooling, acetone (0.5 mL) and ethyl acetate (20 mL) were added. After washing with brine, drying over $MgSO_4$ and concentration, the residue was distilled to give 1,2-diphenylethane as a colourless solid (432 mg, 2.37 mmol, 95%).