RJC Rasayan J. Chem Vol.1, No.2 (2008), 326-330

MICROWAVE ACCELERATED HYDROBORATION OF ALKENES WITH N,N-DIMETHYLANILINE-BORANE

S.V.Jayakumar[1], K. A.Srinivas[2], S.G. Hiriyanna*[3] and Hari N. Pati[4]

[1]Department of Chemistry, University of Madras, Chennai-600032, India
[2]Department of Chemistry, University of Delhi, Delhi-110007, India
[3]DOS in Chemistry, Manasagangothri, University of Mysore, Mysore-570006,India
[4]Department of Chemistry, Sambalpur University, Jyothi Vihar-768019, India
Email: hiriyannag@gmail.com

ABSTRACT

A simple and facile hydroboration-oxidation of alkenes by N,N-dimethylaniline-borane using microwave irradiation is carried out in high yields. The combination of hydroboration with microwave irradiation provided a convenient and rapid method to convert alkenes to alcohols.

***Keywords**: Hydroboration/oxidation, microwave, alkenes, N,N-dimethylaniline-borane.*

INTRODUCTION

Over the decades amine-borane complexes have gained wide applications in synthetic organic chemistry as well as in various industrial applications[1-5]. It has been shown that dialkylarylamines serve as excellent borane carriers[6] and offer several advantages than triethylamine and other alkylamines[7]. For example, dialkylarylamines readily form adducts with borane and these complexes have low sensitivity to moisture and air, and are readily soluble in various solvents. Furthermore, the reactivity of these N,N-dialkylaniline-boranes towards alkenes is shown to be higher than other amine-borane complexes[6].

Although various amine-boranes have been used for hydroboration reactions, the main drawback of these dialkylaniline except diethylaniline and dimethylaniline which are commercially available, as a carrier of borane is that their synthesis. The synthesis of either symmetrical or unsymmetrical dialkylanilines often involves the alkylation of aniline or monoalkylaniline which suffers from various disadvantages such as formation of higher alkylated derivatives, low yields and time consuming[6]. On the other hand, very few reports were available on the use of dimethylaniline-borane as hydroboration reagent as compared to diethylaniline-borane. This is because of less reactivity of the former. The less reactive hydroborating reagents are often require a catalyst to enhance the rate of the hydroboration. Therefore we intended to study the activation of hydroboration of alkenes by less reactive dimethylaniline-borane reagent using microwave irradiation[8].

It has been well studied that the activation of various chemical reactions by microwave irradiation is not only enhances the selectivity and product yield but also decreases the reaction times and undesired side products[9]. Furthermore, with the ease of recovery and recycling of N,N-dialkylamine after the completion of the reaction makes amine-borane complexes as environmentally benign reagents for oxidative transformation of alkenes to alcohols. Hence, we report a simple and facile hydroboration of alkenes activated by microwave irradiation. The oxidation of resulting alkylborane complex with hydrogen peroxide and sodium hydroxide resulted in the corresponding alcohols[10].

EXPERIMENTAL

All hydroboration reactions were carried out under a dry nitrogen atmosphere. All reactions were carried out in domestic microwave at a frequency of 2450 MHz and the power output was 900 W. 1 M Amine-borane stock solution was standardized as following: an aliquot (1 ml) of amine-borane stock solution in dry THF was hydrolysed with 10 ml of 3 N sulphuric acid, liberated volume of hydrogen was calculated. From the volume of hydrogen liberated, the concerntration of borane in the stock solution was calculated.

Typical experimental procedure for hydroboration –oxidation of 1-decene:

An oven dried, 50 ml three-necked round-bottom flask was equipped with microwave reflux condenser connected to a mercury bubbler by means of take-off adapter. Then, 1ml 1-decene (6 mmol) was added followed by amine-borane stock solution in dry THF (6 ml, 2 M solution) by syringe under nitrogen atmosphere. The contents were stirred for about 4 min under microwave irradiation. Then, the reaction mixture was made alkaline by the slow and careful addition of 2 ml of 20% sodium hydroxide. During the addition of alkaline sodium hydroxide solution the contents were cooled followed by the slow addition of 2 ml 35% hydrogen peroxide. The progress of the oxidation reaction was monitored by TLC. Layers were separated and aqueous layer was extracted with diethyl ether (3× 10 ml) organic layers are combined and solvent is removed by vacuum distillation. The hydroboration of other alkenes were performed under similar way.

RESULTS AND DISCUSSION

Hydroboration of various alkenes with N,N-dimethylaniline-borane were carried out in dry THF under specially designed microwave. The microwave was designed in such a way to accommodate magnetic stirrer and refluxing condenser with mercury bubbler. Diborane was prepared by treating the suspension of $NaBH_4$ in THF with dry HCl gas. 1M stock solution of N,N-dimethylaniline-borane complex was prepared treating diborane and N,N-dimethylaniline in dry THF. Hydroboration of simple unhindered alkenes (Table 1, Entry 1, 4, 6, and 11) with N,N-diemthylaniline.borane under microwave irradiation and followed by oxidation with H_2O_2/NaOH was resulted in the formation of corresponding alcohol in 90-95% yield. ^{11}B NMR studies show that hydroboration/oxidation reaction was proceeded via trialkyl-borane complex. [11]. However, the hydroboration of hindered olefins were proceeded upto mono or dialkylborane stage only and subsequent oxidation results in the formation of corresponding alcohol (Table 1, Entry 2, 5, 8, 10, 16, and 17). The formation of mono-, di and trialkyl borane species is confirmed from ^{11}B NMR studies. Monoalkyl-borane species appear at 35 ppm whereas di and trialkyl-borane species appear at 60 ppm and 82 ppm, respectively in ^{11}B NMR.

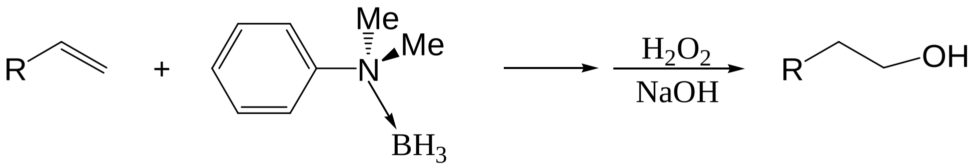


Figure 1: Hydroboration of alkenes with N,N-dimethylaniline-borane**.**

In order to understand the role of microwave irradiation on hydroboration reaction was studied using 1-octene (Table, Entry 11). The hydroboration of 1-octene under microwave irradiation is completed in 4 min whereas the same reaction requires around 8 h to form trialkylborane complex by conventional hydroboration. However, the reaction completes in 2 h at reflux temperature. The easy recovery of the carrier amine from the reaction mixture could result the present method a green process.

Regioselectivity is one of the prime concerns in hydroboration of diene. Hydroboration/oxidation at less substituted double bond predominates over more substituted double bond. In case of 1, 11-diene (Table 1, Entry 14), hydroboration/oxidation was majorily observed at terminal double bond to result (*Z*)-11-alkene-1-ol, which in turn an intermediate compound for synthesis of important pheromones[12,13]. Hydroboration at internal double bond was not at all observed. Similarly, hydroboration/oxidation of limonene (Table 1, Entry 2) was mainly gave 1-hydroxy limenone. The microwave assisted hydroboration-oxidation of various alkenes, dienes, alkynes with N,N-dimethylaniline-borane are presented in Table (1) .

It is noteworthy to mention that the regioselective hydroboration/oxidation of alkenes under microwave irradiation also depends on the ratio between alkene and amine-borane complex. For example, limonene (Table 1, Entry 2) was exclusively hydroborated at exocyclic double bond with 1:3 stoichiometry between amine-borane and alkene. However, with excess of amine-borane complex (1:2), hydroboration of both the double bonds was observed. Similarly 1, 11-diene (Table 1, Entry 14) was hydroborated at teminal dound with less amount of reagent (1:9), but as the amount of reagent is increased to 1:3, hydroboration of terminal as well as internal double bonds were observed.

Hydroboration/oxidation at exo position was favored than endo position in case of norborene via dialkyl-boron species (Table 1, Entry 7). The formation of dialkyl-boron species was also observed in case of cyclohexene and alpha-pinene etc. Alkynes undergo dihydroboration to give 1-alcohol in 90% yield (Table 1, Entry 11). On the other hand, the selective hydroboration of double bond was observed in the presence of alkyne or ester (Table 1, Entry 13 and 15).

In order to understand the efficiency of the borane carrier i.e. N,N-dimethylaniline we also studied the hydroboration of 1-decene with triethyl amine as borane carrier under microwave irradiation. To our surprise, the alkene was not at all hydroborated by triethylamine-borane compex even after 45 minutes irradiation whereas it was completely hydroborated by N,N-dimethylaniline-borane in 4 min.

In summary, environmentally benign, simple versatile method for hydroboration-oxidation of alkenes, dienes and alkynes under microwave irradiation has been explored. The ease of recovery of amine after hydroboration reaction and the possibility of recycling it makes the present method environmentally friendly process.

ACKNOWLEDGEMENTS

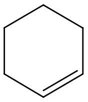
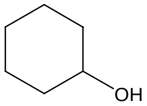
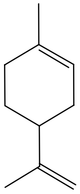
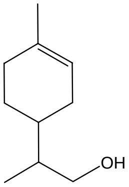
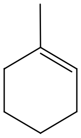
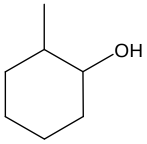
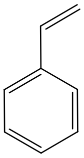
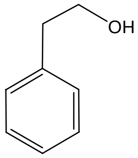
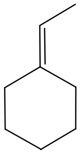
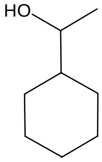
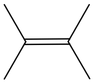
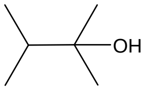
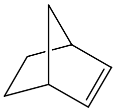
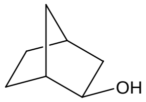
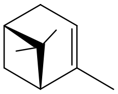
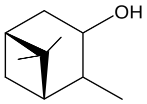
We are thankful to Advinus Therapeutics for help and support.

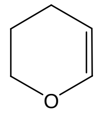
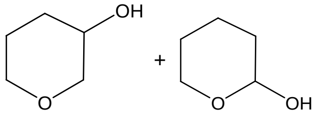
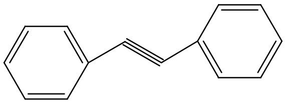
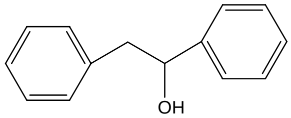
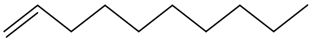
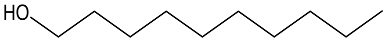
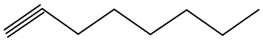
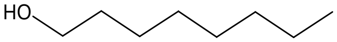
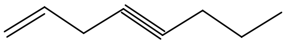
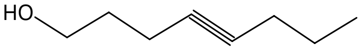
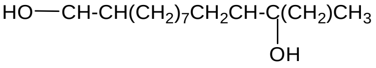
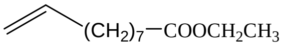
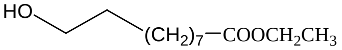
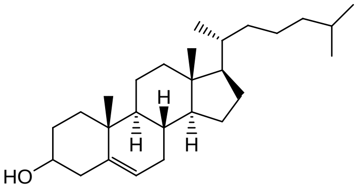
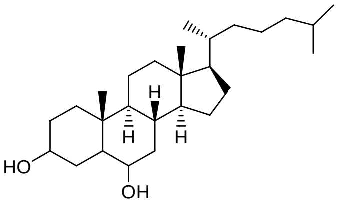
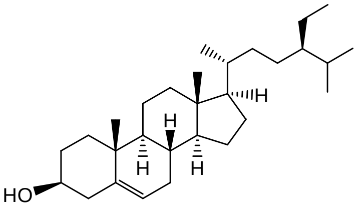
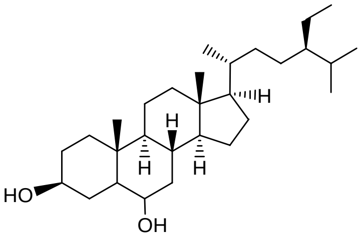
REFERENCES

1. H.C.Brown and B.C.Subba Rao, *J. Org. Chem.*, **22**, 1136 (**1957**).
2. M.F.Hawthorne, *J. Am. Chem. Soc.*, **81**, 5836 (**1959**).
3. H.C.Brown and B.C.Subba Rao, *J. Am. Chem. Soc.*, **78**, 2582 (**1956**)..
4. H.C.Brown and B.C.Subba Rao, *J. Am. Chem. Soc.*, **81**, 6423 (**1959**)..

5. C. F. Lane, *Aldrichimica Acta.*, **6**, 51 (**1973**).
6. J.V.B.Kanth, *Aldrichimica Acta*, **35**, 57 (**2002**).
7. H.C.Brown and L.T.Murray, *Inorg. Chem.*, **23**, 2746 (**1984**).
8. S.W.Hadebe and R.S.Robinson, *Tet. Lett.*, **47**, 1299 (**2006**).
9. F.Mohsenzadeh, K.Aghapoor and H.R.Darabi, *J. Braz. Chem. Soc.*, **18**, 297 (**2007**).
10. C.F.Lane, *J. Org. Chem.*, **39**, 1437 (**1974**).
11. J.A.Akers and T.A.Bryson, *Syn. Comm.*, **20**, 3453 (**1990**).
12. J.Lebreton, K.Draillard and J.Villieras, *Tet. Assym.*, **10**, 4281 (**1999**).
13. S.Narasimhan and R.Balakumar, *Aldrichim. Acta.*, **31**, 1 (**1998**).

Table 1: Hydroboration of various alkenes with N,N-dimethylaniline-borane under microwave irradiation and followed by oxidation with NaOH/H_2O_2

Entry	Reactant	Stoichiometry$^{@}$	Time (min)	Product	% Yield*
1		1:2	3		90
2		1:3	4		89
3		1:2	3		95
4		1:2	4		92
5		1:2	4		95
6		1:1	3		94
7		1:2	4		86
8		1:2	4		90

9		1:2	4		95
10		1:2	4		93
11		1:3	3		94
12		1:2	4		88
13		1:3	4		91
14	$CH_2=CH(CH_2)_7CH_2CH=CH(CH_2)CH_3$	1:9 1:3	4	$HO—C\text{-}CH(CH_2)_7CH_2CH=CH(CH_2)CH_3$ $HO—C\text{-}CH(CH_2)_7CH_2CH=CH(CH_2)CH_3$ +  $HO—CH\text{-}CH(CH_2)_7CH_2CH\text{-}\underset{OH}{C}(CH_2)CH_3$	95 79
15			4		84
16		1:1	4		89
17		1:1	4		93

[@] Stoichiometry ratio is amine-borane : reactant

* Yields were based on GC

(Received: 24 April 2008 Accepted: 2 May 2008 RJC-182)

> **"Learn all you can from the mistakes of others. You won't have time to make them all yourself."**
>
> *-Alfred Sheinwold*