Tetrahedron Letters, Vol. 33, No. 40, pp. 6015-6016, 1992
Printed in Great Britain

0040-4039/92 $5.00 + .00
Pergamon Press Ltd

# Hydroboration of Functionalised Olefins with Acetoxyborohydride

Ranjit S. Dhillon* and Kaushal Nayyar

Department of Chemistry
Punjab Agricultural University
Ludhiana-141 004, India

And

Jasvinder Singh

Department of Chemistry
Panjab University, Chandigarh
India

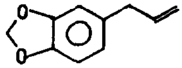
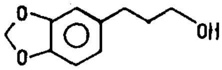
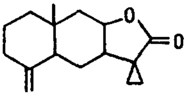
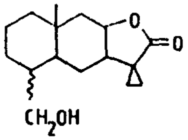
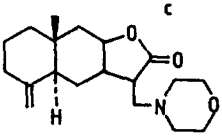
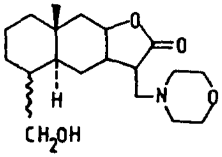
**Abstract :** The acetoxyborohydride has been reported to hydroborate the C = C of functionalised olefins without effecting the functional group.

The development of array of hydroborating reagents[1] mainly from Prof. H.C. Brown's laboratory during the last two decades have immense importance in synthetic methodology as these can selectively hydroborate either a mono or disubstituted double bond of an enyne, or terminal C = C of diene and significantly some of these reagents can also tolerate the functional groups.

Recently, we reported[2] that acetoxyborohydride chemoselectively hydroborates the internal C = C in preference to terminal one and also yield alkyl iodides in enhanced yield over reported in literature[1]. Acetoxyborohydride can be prepared easily from mercuric acetate and sodium borohydride and the coagulation of mercury after reaction work up makes it a cheap hydroborating reagent. Moreover, it is reported[3] to be a mild hydroborating reagent and can tolerate the ester functionality. However, there was no report for hydroboration of carbon-carbon double bond in presence of other functionalities. Thus, this prompted us to explore the hydroboration of various functionalised olefins with acetoxyborohydride. We are gratified to report that this reagent preferentially adds to C = C to afford the corresponding alcohol and does not effect many functional groups as presented in table. However, other carbonyl functionalities do not yield the desired products.

In a typical experimental procedure : the acetoxyborohydride (10 mmole) was prepared in a dry 100 ml flask equipped, under nitrogen, with magnetic stirring bar, septum inlet, and reflux condenser. The flask was charged with sodium borohydride (10 mmole) followed by 20 ml of dry THF. It is then immersed in an ice bath, and 5 mmole of mercuric acetate was added slowly. The contents were allowed to stir for 1 hr at 0°C, brought to room temperature and the functionalised olefin (10 mmole) was added dropwise. The contents were further stirred for 16 hr at room temperature. The oxidation of the resulting organoborane was performed as reported in our previous publication.[2]

Table 1. Hydroboration of Functionalised Olefins

| Entry | Substrate | Product[a] | Isolated yield % |
|---|---|---|---|
| 1. | $CH_2=CH(CH_2)_9CH_2Cl$ | $HOCH_2(CH_2)_{10}CH_2Cl$ | 90 |
| 2. | $CH_2=CH(CH_2)_8CH_2Br$ | $HOCH_2(CH_2)_9CH_2Br$ | 86 |
| 3. | $CH_2=CH(CH_2)_9CH_2I$ | $HOCH_2(CH_2)_{10}CH_2I$ | 85 |
| 4. | $CH_2=CH(CH_2)_8CH_2OTs$ | $HOCH_2(CH_2)_9CH_2OTs$ | 87 |
| 5. | $CH_2=CH(CH_2)_9CH_2OSO_2CH_3$ | $HOCH_2(CH_2)_{10}CH_2OSO_2CH_3$ | 82 |
| 6. | $CH_2=CH(CH_2)_8CON(C_2H_5)_2$ | $HOCH_2(CH_2)_9CON(C_2H_5)_2$ | 81 |
| 7. | $CH_2=CH(CH_2)_8COCl$[b] | $HOCH_2(CH_2)_9COCl$ | 14 |
| 8. |  |  | 91 |
| 9. |  [c] |  | 86 |
| 10. |  [c] |  | 86 |

a Identified by IR, NMR and mass analysis, b 50% excess was used, c During oxidation NaOAc was used instead of NaOH.

**Acknowledgement:** We thank CSIR and ICAR, New Delhi for financial assistance.

**References:**

1. Suzuki, A.; Dhillon, R.S. Top. Curr. Chem. 1986, 130, 23.
2. Gautam, V.K.; Singh, J.; Dhillon, R.S. J. Org. Chem. 1988, 53, 187
3. Narayana, C.; Periasamy, M. Tetrahedron Lett. 1985, 26, 1757.

(Received in UK 22 July 1992)