

Reductive Deoxygenation of Carbonyl to Methylene by $\text{LiAlH}_4/\text{InBr}_3$

Nan Yan FU, Xue Mei ZHAO, Yao Feng YUAN, Ji Tao WANG*

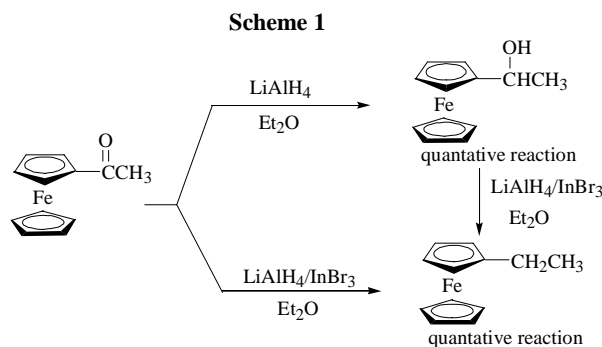
Department of Chemistry, National Key Laboratory of Elemento-organic Chemistry,
Nankai University, Tianjin 300071

Abstract: The reductive deoxygenation of aldehydes and ketones into the corresponding alkanes is accomplished by LiAlH_4 in the presence of Lewis acid InBr_3 . It provides a convenient method to complete the transformation from carbonyl compounds to alkanes.

Keywords: Indium (III) tribromide, lithium aluminium hydride, reductive deoxygenation.

Reductive deoxygenation of aldehyde or ketone leading to the formation of corresponding alkane is a useful synthetic route and can be achieved in various ways¹⁻⁶. Although the Friedel-Crafts alkylation can, in principle, provide the most direct route to the synthesis of alkyl-substituted aromatic compounds, this reaction is known to proceed in poor yields and always produces intricate mixtures of mono- and poly-alkylated derivatives. In contrast, however, the Friedel-Crafts acylation affords excellent yields with a remarkable degree of regioselectivity. So, sometime, we will encounter the transformation of carbonyl group to methylene group in the synthesis of some alkyl-substituted aromatic compounds.

The initial use of LiAlH_4 can be updated to 1947^{7,8} and now it becomes one of the most common reducing agents in various organic reactions. Although LiAlH_4 can reduce almost all carbonyl groups containing oxygen to the corresponding alcohols, it can not further complete the transformation from alcohols to corresponding alkanes.



* E-mail: wangjt@nankai.edu.cn

In our work, we found that the reductive ability of the LiAlH_4 was enhanced in the presence of InBr_3 . Adding stoichiometric InBr_3 to the reaction mixture, acetylferrocene was reduced to ethylferrocene quantitatively. Further research showed that stoichiometric InBr_3 was requisite, otherwise, a mixture of ethylferrocene and 1-hydroxyethylferrocene were obtained and the ratio of these two compounds had direct relationship with the amount of InBr_3 under the same reaction conditions. Furthermore, 1-hydroxyethyl ferrocene can also be reduced to ethylferrocene thoroughly (**Scheme 1**).

We also extended this reducing agent into the reduction of aromatic/aliphatic aldehydes and ketones. The results are listed in **Table 1**. The reductive deoxygenation of aldehydes and ketones mediated by $\text{LiAlH}_4/\text{InBr}_3$ reductive system proceeds very smoothly to give the corresponding alkanes with satisfactory to moderate yield under mild conditions.

Table 1 The Results of Reduction under $\text{LiAlH}_4/\text{InBr}_3$

Substrate	Substrate: LiAlH_4 : InBr_3 (mol: mol: mol)	Refluxing time (hr)	Yield of alkane (%)
Acetophenone	1:1:1	5	56 ^a
Benzaldehyde	1:1:1	6	59 ^a
<i>o</i> -Methyl-benzaldehyde	1:1:1	7	36 ^a
<i>p</i> -Chloro-benzaldehyde	1:1:1	9	23 ^a
Hexanal	1:1:1	7.5	48 ^b
Cyclohexanone	1:1:1	7.5	82 ^b

^a The yield was determined by HPLC. ^b The yield was determined by GC.

General Procedure

Under an inert atmosphere of nitrogen, LiAlH_4 (0.076 g, 2 mmol) and InBr_3 (0.709 g, 2 mmol) was added into 20 mL absolute ether in an ice bath. After stirring for 30 min in ice bath, 2 mmol aldehyde or ketone was added. Then, the reaction mixture was refluxed for several hours under stirring. After that, the mixture was poured onto 20 g ice to quench the reaction and extracted with ether (3×15 mL). The organic layer was washed with brine, dried over anhydrous MgSO_4 . The solvent was removed and the residue was analyzed by GC or HPLC.

Acknowledgment

We thank the National Natural Science Foundation of China (29872018 & 29972026), the Key Laboratory of Elemento-organic Chemistry, Nankai University and RFDP, China's Ministry of Higher Education (1999005520) for their financial support.

References

1. A. Srikrishna, R. Viswajanani, J. A. Sattigeri, C. V. Yelamaggad, *Tetradron. Lett.*, **1995**, *36*, 2347.
2. E. N. Alesso, D. E. Bianci, L. M. Finkielszein, B. Lantano, G. Y. Moltrasio, Aguirre, *Tetrahedron Lett.*, **1995**, *36*, 3299.
3. V. G. S. Box, P. C. Meleties, *Tetrahedron. Lett.*, **1998**, *39*, 7057.

**Reductive Deoxygenation of Carbonyl to Methylene by
LiAlH₄/InBr₃**

4. T. Miyai, M. Ueba, A. Baba, *Synlet.*, **1999**, 182.
5. J. M. Khurana, A. Ray, S. Singh, *Tetrahedron. Lett.*, **1998**, 39, 3829.
6. W. Baik, H. J. Lee, S. Koo, B. H. Kim, *Tetrahedron. Lett.*, **1998**, 39, 8125.
7. A. E. Finholt, A. C. Bond Jr., H. I. Schledinger, *J. Am. Chem. Soc.*, **1947**, 69, 1199.
8. R. F. Nystron, W. G. Browm, *J. Am. Chem. Soc.*, **1947**, 69, 1167.

Received 10 December, 2001

Revised 19 November, 2002