SYNLETT Spotlight 287

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research

DABAL-Me₃: A Versatile Methylating Agent

Compiled by Abhishek Goswami

Abhishek Goswami was born in Jorhat, Assam, India, in 1981. He completed his B.Sc. degree in 2002 at the Dibrugarh University and M.Sc. degree in 2005 at the Gauhati University, Assam, India, with specialization in Physical Chemistry. At present, he is working towards his Ph.D. degree at Natural Products Chemistry Division, North-East Institute of Science & Technology (CSIR), Jorhat, Assam, India, under the guidance of Dr. Nabin C. Barua. His area of research interest is partial and total synthesis of natural products of biological significance and development of new synthetic methodologies for target oriented synthesis.

Natural Products Chemistry Division, North-East Institute of Science & Technology, Jorhat-785 006, Assam, India E-mail: abhijrt@yahoo.com

riety of substrates.



This document was downloaded for personal use only. Unauthorized distribution is strictly prohibited.

Introduction

DABAL-Me₃ is a very suitable, easy to use reagent to methylate a variety of functional groups like aldehydes, imines, enones, amides, etc. Although trimethyl aluminium has been traditionally used as a methylating agent, its pyrophoric nature stands as a major obstacle in its sustainability. Several other Me₃Al·NR₃ species such as Me₃Al·pyridine, Me₃Al·TMEDA (tetramethyletyhylenediamine) are also reported, but they are too reactive to be used under normal laboratory conditions. DABAL-Me₃,

Abstracts

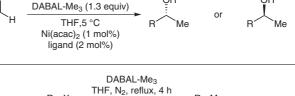
(A) Woodward and co-workers reported the first assymmetric synthesis of secondary alchohols from prochiral aldehydes in the presence of nickel(acetylacetone)₂ and a phosphoroamidite ligand.³ R

(B) Methylation of aryl and vinyl halides is another example of a very efficient route of forming C–C bonds. DABAL-Me₃ is quite capable of carrying out this transformation.⁴

(C) In pursuance of developing a suitable route for addition of an alkyl group to different Michael acceptors, Woodward and co-workers used DABAL-Me₃ in an enantioselective manner employing appropriate ligands.⁵

(D) Direct formation of amides from the corresponding inactivated esters and lactones can be conveniently carried out with DABAL-Me₃ excluding the risk of using other pyrophoric AlR₃ reagents.⁶ Woodward and co-workers later utilized microwave irradiation in DABAL-Me₃-mediated amide bond formation in order to carry out the reaction in a shorter span of time.⁷

SYNLETT 2009, No. 13, pp 2203–2204 Advanced online publication: 23.07.2009 DOI: 10.1055/s-0029-1217623; Art ID: V29309ST © Georg Thieme Verlag Stuttgart · New York



which is actually a 2:1 complex of Me_3Al and DABCO, is free from these shortcomings as it can be manipulated

DABAL-Me₃ can be prepared by adding neat AlMe₃ to

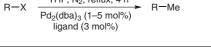
freshly sublimed DABCO in toluene at 0 °C. The white

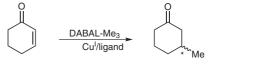
precipitate is separated from toluene and washed several

times with diethyl ether.³ The versatility of the reagent can

be easily assessed by its capability to methylate a wide va-

without the need for an inert atmosphere.^{1,2}







References

- (1) Bradford, A. M.; Bradley, D. C.; Hursthouse, M. B.; Motevalli, M. *Organometallics* **1992**, *11*, 111.
- (2) Woodward, S. Synlett 2007, 1490.
- (3) Biswas, K.; Prieto, O.; Goldsmith, P. J.; Woodward, S. Angew. Chem. Int. Ed. **2005**, 44, 2232.
- (4) Cooper, T.; Novak, A.; Humphreys, L. D.; Walker, M. D.; Woodward, S. Adv. Synth. Catal. 2006, 348, 686.
- (5) Alexakis, A.; Albrow, V.; Bisaws, K.; d'Augustin, M.; Prieto, O.; Woodward, S. *Chem. Commun.* **2005**, 2843.
- (6) Novak, A.; Humphreys, L. D.; Walker, M. D.; Woodward, S. *Tetrahedron Lett.* **2006**, *47*, 5767.
- (7) Glynn, D.; Bernier, D.; Woodward, S. *Tetrahedron Lett.* 2008, 49, 5687.