

SYNLETT Spotlight 26

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

Methylaluminium bis(4-substituted-2,6-di-*tert*-butylphenoxide): MAD and MABR Lewis acids

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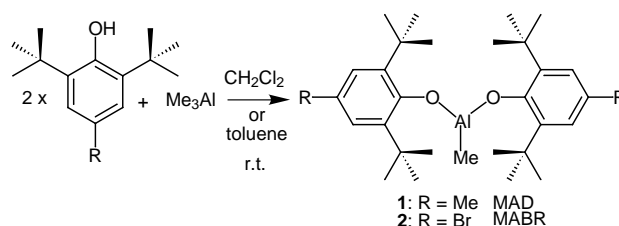
Cyril Papamicaël obtained his PhD under the guidance of Professor G. Quéguiner and G. Dupas at the University of Rouen (France) in 1997. He then spent two years working with Professor A. Gossauer at the University of Fribourg (Switzerland). He is currently engaged in a postdoctoral work with Professor C.J. Schofield at the University of Oxford (United-Kingdom).



Methylaluminium bis(4-substituted-2,6-di-*tert*-butylphenoxide) MAD **1** and MABR **2** are bulky aluminium Lewis acids introduced into organic synthesis by Yamamoto et al.¹ They proved to be very versatile reagents. Examples include all kinds of reactions such as radical reaction,² cycloaddition,³ carbonyl *ene* reaction,⁴ Mukaiyama aldol reaction,⁵ rearrangement of epoxides to prepare aldehydes⁶ and *anti*-Cram carbonyl alkylation.^{1a}

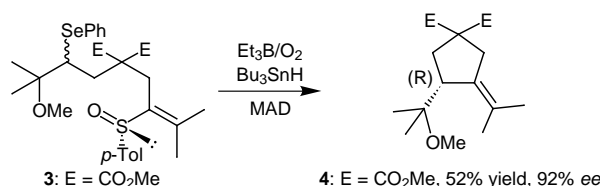
Preparation: The MAD and MABR reagents are easily prepared from the corresponding commercially available

phenols by treatment with methylaluminium for 1 hour.^{6,7} No purification is required but MAD and MABR are inflammable and must be handled in the absence of air and moisture.

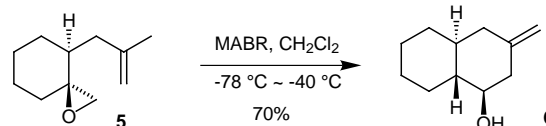


Abstracts

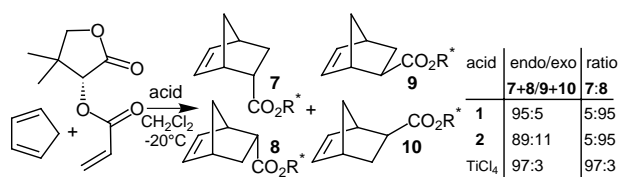
(A) In the presence of the MAD Lewis acid, which complexes to the oxygen atom of the sulfoxide group, the radical cyclization/ β -elimination tandem reaction leads to the R enantiomer **4**. Without the MAD reagent, the S enantiomer is isolated (93% yield, >96% *ee*).²



(B) A general method of six-membered carbocycles has been demonstrated, which involves the stereo-controlled cyclization of olefinic epoxides with MABR via the epoxide rearrangement and subsequent intramolecular *ene* reaction with high stereoselectivity.⁷ Treatment of **5** with MABR afforded *trans*-decalin-1-ol **6** as a sole isolable product with rigorous stereochemistry in 70% yield.



(C) The MAD **1** or MABR **2** can be successfully utilised as a highly efficient nonchelating Lewis acid for achieving high stereoselectivity in 1,*n* asymmetric induction in cyclic as well as acyclic systems. Thus, Diels-Alder reaction of the acrylate of D-pantolactone and cyclopentadiene exhibits high diastereoselectivity not observable with ordinary Lewis acids.³



References and Notes

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