Trimethylaluminium

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Sammy Drissi-Amraoui was born in Bressuire, France in 1990. In 2011, he worked as a one-year student in the Chemistry Department of Merck Serono, Geneva, under the supervision of Dr. Cyril Montagne and Dr. Dominique Swinnen, working on photochemistry for the synthesis of drug-like compounds. In 2013, he graduated from the Ecole Nationale Supérieure de Chimie de Montpellier (ENSCM) in organic chemistry and received his M.Sc. in chemistry of biomolecules for health. He started his Ph.D. studies in 2013 under the supervision of Prof. Jean-Marc Campagne and Dr. Renata Marcia de Figueiredo and his research focuses on asymmetric conjugate additions and total synthesis.

Introduction

Trimethylaluminium (or trimethylaluminum, TMA) [CAS Reg. No. 75-24-1] is an organometallic reagent from the family of alanes, described first in 1939. This highly pyrophoric compound is a liquid at room temperature (mp 15 °C) and is commercialized neat or as a solution in an organic solvent (hexane, heptane, toluene, chlorobenzene).

This versatile reagent has a high Lewis acid character, much more than zinc or magnesium organometallic compounds. In addition, the reagent is used as methyl nucleophilic donor, the cheapest one thanks to its industrial use.

Table 1 Use of Trimethylaluminium

(A) Gremaud and Alexakis accomplished the copper-catalyzed enantioselective 1,4-addition of TMA on β1,γ-unsaturated α-keto esters. The reaction was performed with excellent 1,4-regioselectivity, yield, and enantiomeric excess only with the simple commercially available ligand BINAP.

(B) Alternatively to the well-known zirconium-catalyzed carbometalation of alkynes, a new regio- and stereospecific scandium-catalyzed methodology was employed by Hou and co-workers.

(C) The Cu-catalyzed enantioselective conjugate addition of a β-alkenylationaluminium reagent (prepared via Ni catalysis) to an α,β-unsaturated ketone (which is issued by Zr-catalyzed carboalumination using TMA) was reported by McGrath and Hoveyda. This multicomponent reaction allowed the enantioselective synthesis of β,β-disubstituted ketones from alkynes.

This reagent can be prepared, amongst other methods, from aluminium and chloroform, dimethylaluminium chloride or methylaluminium sesquichloride, treated with sodium or sodium/potassium. The preparation has been industrialized above all by Ziegler, who later reported the Ziegler–Natta polymerization with TMA.
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References

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