SYNLETT Spotlight 1

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

Bis(cyclopentadienyl)titanium(III) Chloride¹

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Bis(cyclopentadienyl)titanium(III) chloride **1** - Nugent's reagent - exists as a chloride-bridged dimer in its solid state, but dissociates to its monomeric species in the presence of donor solvents (eg. THF) to afford a loosely solvated 'transition-metal-centred-radical'. The very mild nature of Nugent's reagent, and its selective one-electron reduction of epoxides results in its compatibility with highly functionalised compounds. The reactivity of the carbon-centred radical formed by initial C-O homolysis of the epoxide can be tuned depending on the reacting partner.

Preparation: (comparable yields have been obtained for reactions using the in situ reagent versus isolated Cp₂TiCl)

1) Isolated Cp₂TiCl (yellowish green solid) is prepared by the treatment of titanium(III) chloride with thallium cyclopentadienide.²

2) In situ Cp₂TiCl (lime green solution) is prepared quantitatively from titanocene dichloride and powdered zinc in THF.¹

Abstracts

A) The deoxygenation of methyl furanoside **2** to its corresponding olefinic product **3** has been the target of extensive synthetic efforts. The mildness of this deoxygenation procedure is attested by the fact that even the acidic impurities in CDCl₃ are sufficient for conversion to the fully aromatic product.³

B) The stereoselective total synthesis of (+/-)-methylenolactocin **4** used Nugent's reagent in the key intramolecular epoxyheptyne radical cyclisation step.⁴

C) The intramolecular addition of epoxides to activated olefins utilizes Nugent's reagent to effect homolysis of the epoxide C-O bond. The δ-hydroxy ester formed on work-up cyclises to the spirolactone **5**.⁵ (Interestingly, under the reaction conditions no further addition or polymerisation of methyl methacrylate occurred)

References

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