SYNLETT SPOTLIGHT

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) Chloride

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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

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\begin{align*}
\text{TiCl}_3 + 2\text{CpTiCl} & \rightarrow \text{Cp}_2\text{TiCl} + 2\text{TiCl} \\
2\text{Cp}_2\text{TiCl}_2 + \text{Zn} & \rightarrow 2\text{Cp}_2\text{TiCl} + \text{ZnCl}_2
\end{align*}
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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

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 spirilactone 5.⁵ (Interestingly, under the reaction conditions no further addition or polymerisation of methyl methacrylate occurred)

References