SYNLETT Spotlight 51

Cerium(III) Chloride Heptahydrate: $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$

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

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Introduction

Few areas of synthetic chemistry have witnessed a growth as explosive as that brought about by the application of lanthanide reagents to organic synthesis. Cerium(III) chloride heptahydrate¹ is a commercially available lanthanide reagent which is water tolerant, non-toxic, easy to handle, inexpensive and can be used without further purification.

Abstracts

A) Luche² used the combination of CeCl_3 and NaBH_4 for selective reduction of conjugated aldehydes and ketones to allylic alcohols. This procedure has general utility and has been embraced by the synthetic organic chemistry community for 1,2 reduction of enones where other reagents (eg. DIBAL-H, LiAlH_4 , $\text{Zn}(\text{BH}_4)_2$ or NaBH_4 alone) failed to provide the described products or gave inferior results.

Similarly, selective reduction of ketones in the presence of aldehydes⁵ and selective ketalization of aldehydes in the presence of ketones⁶ were also very effective using CeCl_3 . In another report, reduction of conjugated cyclohexenones was achieved using NaBH_4 - $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ in aliphatic alcohols.⁷

B) Cerium(III) chloride was shown to catalyze the Michael addition⁴ of 1,3 dicarbonyl compounds to α,β -unsaturated ketones and α,β -unsaturated aldehydes in the presence of NaI. The catalyst system can be easily separated from the reaction mixture and it can be reused without an appreciable loss of activity. The reactions can also be performed without solvents under microwave irradiation.⁸

C) Cerium(III) chloride is a novel reagent for the nonaqueous selective conversion of dioxolane to carbonyl compounds.⁹ Similarly, $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ -NaI in acetonitrile has been recently reported for the selective deprotection of the *tert*-butyl esters in the presence of *N*-Boc protecting group.¹⁰

D) Highly regioselective ring opening of epoxides and aziridines has been carried out using cerium(III) chloride to synthesize the corresponding chlorohydrins,¹¹ iodohydrins,¹¹ 1,2-azidoalcohols,¹² 1,2-aminoalcohol,¹³ chloroamines,¹¹ iodoamines¹¹ and 1,2-azidoamines.¹²

E) Cerium(III) chloride has been used as a mild Lewis acid, and efficient catalyst for the deprotection of alcohol protecting groups such as MEM,¹⁴ Tr,¹⁵ TBDMS,¹⁶ allyl,¹⁷ prenyl,¹⁸ Me¹⁸ and PMB.¹⁹

A simple and efficient method for the conversion of alcohols into alkyl iodides²⁰ using $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ –NaI system in acetonitrile has been reported.

F) α, α' -Dibromo ketones react with 1,3-dienes in the presence of CeCl_3 – SnCl_2 , providing [3+4] cycloadducts via the oxyallyl cation intermediate.²¹

G) Organocerium reagents²² are generated in situ by transmetalation reactions from organolithium²³ or organomagnesium reagents.⁴ Organocerium reagents are highly oxophilic and significantly less basic than their RLi and RMgBr counterparts.

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