SYNLETT SPOTLIGHT 722

SYNLETT Spotlight 29

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

Chromium(II) Chloride: CrCl₂

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Rachid Baati was born in 1972 in Oued-zem, (Morocco). He studied at the Université Louis Pasteur in Strasbourg, then at the Ecole Nationale Supérieure de Chimie de Strasbourg (EHICS-ECPM). Currently he is finishing his Ph.D thesis under the direction of Dr Charles Mioskowski at the Faculté de Pharmacie de Strasbourg.



Since the discovery of Nozaki and Hiyama¹ in 1977, who found that Cr(II) ion promotes chemoselective C-C coupling in aprotic solvents, extensive studies has been devoted to organochromium(III) reagents. These compounds are prepared by oxidative insertion of CrCl₂ into allyl, alkenyl, alkynyl, propargyl and aryl halides or sulfonates which are well behaved nucleophiles for highly selective organic transformations.

Recently, Fürstner² has demonstrated that these reactions could be performed with a catalytic amount of CrCl₂ or CrCl₃. Chromium chloride reagent is commercially available and can be used without further purification. It is very hygroscopic, stable in dry air but oxidizes rapidly in the presence of oxygen. Anhydrous chromous chloride could be prepared by the reduction of CrCl₃ with LiAlH₄¹ or other suitable reducing agents.⁷

Abstracts

Highly stereoselective synthesis of homoallylic alcohols³ have been carried out by the use of Nozaki-Hiayma reaction in the presence of the (R,R)-*N*,*N*'-bis(3,5-di-*tert*-butyl-salicylidene)-1,2-cyclohexanediamine (salen).

This important reaction has recently been extended to halogenated allylic substrates.⁴ This reaction provides a new route for the preparation of quaternary halogenated carbons.

The reaction of haloform with an aldehyde mediated by CrCl₂ leads to the formation of an *E*-configured halogenated double bond (Takai reaction).⁵ A geminal organodichromium species is expected to be the reactive intermediate.

$$XCHHal_2 \xrightarrow{CrCl_2} \begin{bmatrix} Cr^{|||} \\ Cr^{|||} \end{bmatrix} \xrightarrow{R} H \xrightarrow{RCHO} R$$

 $X = CI, Br, I, SnR_2, SiR_3, SPh, B(OR)_2$

E-olefine

Besides C-C bond formation, CrCl₂ can also mediate efficiently the protection of a plethora of alcohols as their corresponding 2-tetrahydrofuranyl ethers.⁶

R=OH
$$\frac{\text{CrCl}_2, \text{ rt}}{\text{THF/CCl}_4}$$
 R= alkyl, aryl 47-95%

References and Notes

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Article Identifier: 1437-2096,E;2001,0,05,722,722,ftx,en;V03000ST.pdf