SYNLETT
Spotlight 64

Zirconium Tetrachloride
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The use of transition metal salts in organic synthesis is an emerging area of research. Due to their low toxicity (LD₅₀ [ZrCl₄, oral rat] = 1688 mgKg⁻¹),¹ low cost, ease of handling, and high catalytic activity, the Zr(IV) compounds are potential green catalysts. ZrCl₄ is a relatively weak Lewis acid,² which finds uses in Friedal–Crafts reaction,³ Diels–Alder reactions,⁴ asymmetric Diels–Alder reaction,⁵ [2+2]-adduct formation,⁶ and intramolecular cyclization.⁷ The application of ZrCl₄ in organic reactions is gaining renewed interests.

Zirconium tetrachloride may be prepared by chlorination of heated zirconium, zirconium carbide, or a mixture of ZrO₂ and charcoal.⁸

Abstract

(A) ZrCl₄ facilitates a high yielding homologation of ketones into α-methoxy ketones⁹ via intermediate sulfone adducts. This procedure allows the sulfone mediated homologation methodology to be applied to monocyclic and acyclic ketones.

(B) ZrCl₄/NaBH₄ reduces¹⁰ various functional groups including carbonyls, olefins, imines, and nitriles. The above reducing system along with a chiral amino alcohol have been successfully applied to the enantioselective reduction of oxime ethers.¹¹ ZrCl₄ in the presence of NaBH₄ and (S)(−)-α,α-diphenyl prolinol catalyzed the enantioselective reduction of prochiral ketones with moderate to high enantiomeric excess.¹²

(C) ZrCl₄ is an excellent mediator of the Fries reaction¹³ and it transforms 6-methoxytetralins into 8-methoxytetralins.¹⁴ The Fries rearrangement occurs at ambient temperature and is highly selective with preferential migration towards the least sterically encumbered adjacent carbon centre. Use of ultrasound in this reaction is often beneficial.

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(D) ZrCl₄ catalyzed the hydrostannation of acetylenes by tributyltin hydride to produce the cis-vinylstannanes by regio- and stereoselective anti-hydrostannation. The hydrostannation of acetylene using dibutyltin dihydride is also catalyzed by ZrCl₄ to give the stereodefined Z-Z divinyltin derivatives by an anti-hydrostannation pathway. This reaction at 0 °C gave better yields and stereoselectivity than the reaction at room temperature. The trans-allylstannylation of simple acetylenes is also catalyzed by ZrCl₄ to produce alkenylstannanes in a regio- and stereoselective manner.

(E) ZrCl₄ is an effective catalyst for highly chemoselective trans-thioacetalization of acetals under mild reaction condition. High rates of reaction, mild reaction conditions, high chemoselectivity, easy work-up and high yields of the desired product highlight this reaction.

(F) ZrCl₄ is an efficient catalyst for the synthesis of α-aminophosphates. The method is effective for aromatic, aliphatic, or α,β-unsaturated aldehydes and provides excellent yields of the product.

(G) The THF complex of ZrCl₄, i.e. ZrCl₄(THF)₂, is highly effective as a catalyst for the selective esterification of primary alcohols with carboxylic acids in the presence of secondary alcohols or aromatic alcohols. Direct condensation of equimolar amounts of carboxylic acids and alcohols could be achieved using Zr(IV) salts. This method offers considerable advantage in terms of simplicity, high chemoselectivity, high atom efficiency, and low environmental impact.

References