SYNLETT Spotlight 77

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

Gallium Trichloride

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Introduction

Like some of the other group 13 trihalides (not Al, In, and Tl), galliumtrichloride has a (bridged dimer) molecular lattice as shown (Figure 1).

The dimer molecules are arranged in sheets. The low intermolecular forces are responsible for the low mp (77.9 °C, the lowest of the Al, Ga, In, and Tl trihalides).¹

GaCl₃ is evidently a weaker acid than AlCl₃. Its application in organic synthesis has been known for a long time e.g. in the Friedel–Crafts synthesis of benzophenone from benzene and benzoyl chloride GaCl₃ results in a faster reaction than AlCl₃,² the reaction of benzene with alkyl halides is also quicker with gallium.³

Preparation

GaCl₃ is available commercially or can be prepared by burning gallium in a stream of Cl₂,^{4,5} or by the action of HCl or SOCl₂ (> ca 200 °C) Ga₂O₃.^{4,6} The pure anhydrous compound can be obtained by redistillation in a steam of Cl₂ (or Cl₂/N₂) followed by vacuum sublimation or by zone refining.⁴

Abstracts

(A) In the presence of GaCl₃, silyl enol ethers are ethynylated at the α -carbon atom with chlorotrimethylsilyl ethyne to give α -ethynylated aryl ketones possessing α -protons without isomerization to conjugated allenyl ketones.⁷

(B) Trimethylsilyl ethyne and silyl enol ether were reacted with GaCl₃ in methylcyclohexane at r.t. and after treatment with THF and 6 M H₂SO₄, α -ethenyl ketone was obtained in high yield. Employment of GaCl₃ was essential, and no reaction occurred with AlCl₃, InCl₃, or other Lewis acids of group 13 elements.⁸

(C) Treatment of alkynes with allyl trimethyl silanes in the presence of GaCl₃ gives 1,4-dienes via allylgallation.⁹

(D) Treatment of aryl halides with alkenyl gallium dichloride, prepared from GaCl_3 and alkenyl magnesium bromide, in the presence of a catalytic amount of palladium provided cross-coupling product in good yield.¹⁰

(E) GaCl_3 catalyzes the tandem ring opening of epoxides and cyclization with alkynes to generate naphthalene derivatives with complete regiocontrol.¹¹

(F) In the presence of GaCl_3 , silyl enol ethers derived from substituted ketoesters or malonates are ethenylated at the carbon atom with trimethylsilyl ethyne in high yields. Ethenylmalonates can also be synthesized by this method.¹²

(G) A gallium hydride reagent, HGaCl_2 , was found to act as a radical mediator, like Bu_3SNH . Treatment of alkyl halides with HGaCl_2 , generated from GaCl_3 and sodium bis-(2-methoxyethoxy)aluminum hydride, provided the corresponding reduced products in excellent yields. Radical cyclization of halo-acetals was also successful with both a stoichiometric amount of gallium reagent but also a catalytic amount of GaCl_3 combined with a stoichiometric amount of AlH_3 as a hydride source.¹³

(H) Alkenyl Fischer chromium carbene complexes react with various kinds of simple imines to produce 3-pyrroline derivatives in the presence of a catalytic amount of GaCl_3 .¹⁴

(I) The allylgallium reagent which may be prepared by mixing GaCl_3 and an equimolar amount of allylmagnesium chloride, allylated carbonyl compounds in good yields in aqueous media and organic solvents.¹⁵

(J) (Trimethylsilyl)acetylene upon treatment with GaCl_3 in CH_2Cl_2 and methylcyclohexane, trimerized rapidly giving acyclic conjugated trienes.¹⁶

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