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), gallium trichloride has a (bridged dimer) molecular lattice as shown (Figure 1).

The dimmer 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).\(^1\) GaCl\(_3\) is evidently a weaker acid than AlCl\(_3\). 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 GaCl\(_3\) results in a faster reaction than AlCl\(_3\),\(^2\) the reaction of benzene with alkyl halides is also quicker with gallium.\(^3\)

Preparation

GaCl\(_3\) is available commercially or can be prepared by burning gallium in a stream of Cl\(_2\)\(^4,5\) or by the action of HCl or SOCl\(_2\) (> ca 200 °C) Ga\(_2\)O\(_3\).\(^4,6\) The pure anhydrous compound can be obtained by redistillation in a stream of Cl\(_2\) (or Cl\(_2\)/ N\(_2\)) followed by vacuum sublimation or by zone refining.\(^7\)

Abstracts

(A) In the presence of GaCl\(_3\), silyl enol ethers are ethynylated at the \(\alpha\)-carbon atom with chlorotrimethylsilyl ethyne to give \(\alpha\)-ethynylated aryl ketones possessing \(\alpha\)-protons without isomerization to conjugated allenyl ketones.\(^7\)

(B) Trimethylsilylethylene and silyl enol ether were reacted with GaCl\(_3\) in methylcyclohexane at r.t. and after treatment with THF and 6 M H\(_2\)SO\(_4\), \(\alpha\)-ethenylketone was obtained in high yield. Employment of GaCl\(_3\) was essential, and no reaction occurred with AlCl\(_3\), InCl\(_3\), or other Lewis acids of group 13 elements.\(^8\)

(C) Treatment of alkynes with allyl trimethyl silanes in the presence of GaCl\(_3\) gives 1,4-dienes via allylgallation.\(^9\)
(D) Treatment of aryl halides with alkenyl gallium dichloride, prepared from GaCl3 and alkenyl magnesium bromide, in the presence of a catalytic amount of palladium provided cross-coupling products in good yield.\[10\]

(E) GaCl3 catalyzes the tandem ring opening of epoxides and cyclization with alkynes to generate naphthalene derivatives with complete regiocontrol.\[11\]

(F) In the presence of GaCl3, silyl enol ethers derived from substituted ketoesters or malonates are ethenylated at the carbon atom with trimethylsilyl ethylen in high yields. Ethenylmalonates can also be synthesized by this method.\[12\]

(G) A gallium hydride reagent, HGaCl2, was found to act as a radical mediator, like Bu3SNH. Treatment of alkyl halides with HGaCl2, generated from GaCl3 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 GaCl3 combined with a stoichiometric amount of AlH3 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 GaCl3.\[14\]

(I) The allylgallium reagent which may be prepared by mixing GaCl3 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 GaCl3 in CH2Cl2 and methylcyclohexane, trimerized rapidly giving acyclic conjugated trienes.\[16\]

References

(2) Id. Z. Electrochemistry 1935, 41, 509.
(3) Ulrich, H. Angew. Chem. 1942, 55, 37.