

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

Compiled by Dhiren Chandra Barman

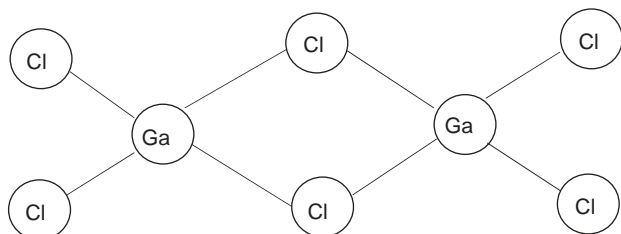
Dhiren Chandra Barman was born in 1976 and received his MSc degree (Chemistry) in 1999 from Gauhati University, Assam, India. Thereafter he joined Dr. J. S. Sandhu's group in the Medicinal Chemistry Division of the Regional Research Laboratory (CSIR) Jorhat, Assam, India. His PhD focused on cycloaddition reactions for the synthesis of novel heterocycles of biological significance and some functional group transformations. After submitting his thesis he continued to study cycloaddition reactions with Dr. D. Prapapati Sc. E II at the same institute. Presently he is working in Dr. Reddys Laboratory, Hyderabad, India.

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Introduction

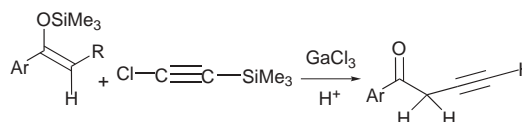
Like some of the other group 13 trihalides (not Al, In, and Tl), galliumtrichloride has a (bridged dimer) molecular lattice as shown (Figure 1).



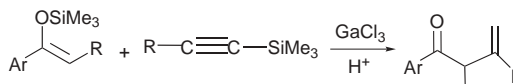
The dimer molecules are arranged in sheets. The low intermolecular forces are responsible for the low mp (77.9 °C, the lowest of the Al, Ga, In, and Tl trihalides).¹

Abstracts

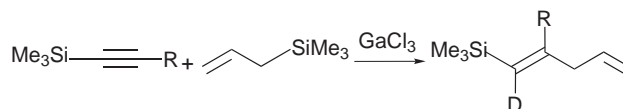
(A) In the presence of GaCl_3 , silyl enol ethers are ethynylated at the α -carbon atom with chlorotrimethylsilyl ethyne to give α -ethynylated aryl ketones possessing α -protons without isomerization to conjugated allenyl ketones.⁷



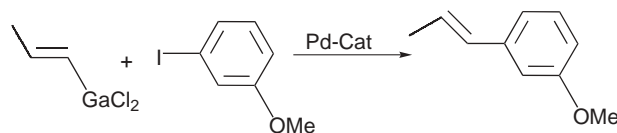
(B) Trimethylsilylethyne and silyl enol ether were reacted with GaCl_3 in methylcyclohexane at r.t. and after treatment with THF and 6 M H_2SO_4 , α -ethenyl ketone was obtained in high yield. Employment of GaCl_3 was essential, and no reaction occurred with AlCl_3 , InCl_3 , or other Lewis acids of group 13 elements.⁸



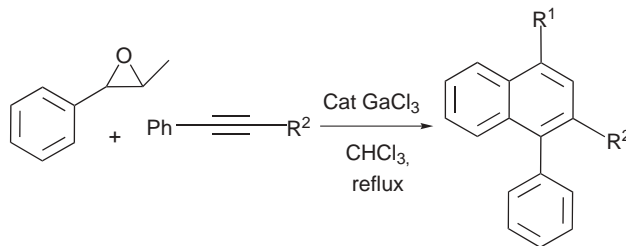
(C) Treatment of alkynes with allyl trimethyl silanes in the presence of GaCl_3 gives 1,4-dienes via allylgallation.⁹



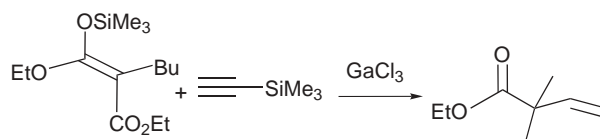
(D) Treatment of aryl halides with alkenyl gallium dichloride, prepared from GaCl₃ and alkenyl magnesium bromide, in the presence of a catalytic amount of palladium provided cross-coupling product in good yield.¹⁰



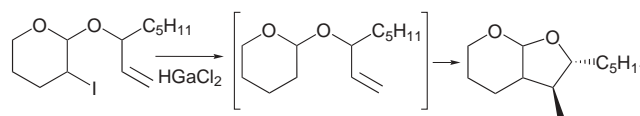
(E) GaCl₃ catalyzes the tandem ring opening of epoxides and cyclization with alkynes to generate naphthalene derivatives with complete regiocontrol.¹¹



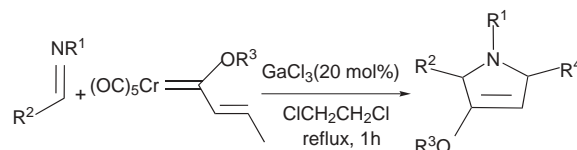
(F) In the presence of GaCl₃, silyl enol ethers derived from substituted ketoesters or malonates are ethenylated at the carbon atom with trimethylsilyl ethyne in high yields. Ethenylmalonates can also be synthesized by this method.¹²



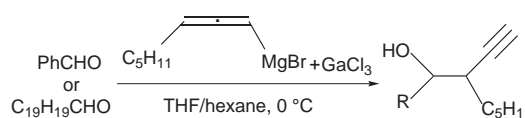
(G) A gallium hydride reagent, HGaCl₂, was found to act as a radical mediator, like Bu₃SNH. Treatment of alkyl halides with HGaCl₂, generated from GaCl₃ and sodium bis-(2-methoxyethoxy)aluminum hydride, provided the corresponding reduced products in excellent yields. Radical cyclization of halo-acetals 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



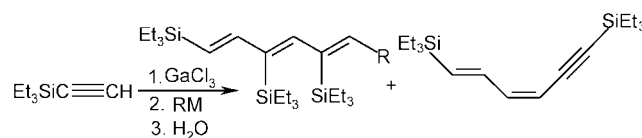
(H) Alkenyl Fischer chromium carbene complexes react with various kinds of simple imines to produce 3-pyrroline derivatives in the presence of a catalytic amount of GaCl₃.¹⁴



(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

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