Malononitrile

Compiled by Anil Saikia

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The weak cyanocarbon malononitrile \([\text{CH}_2(\text{CN})_2]\) is a colourless solid with a melting range of 32–34 °C and a boiling range of 218–219 °C. It is a versatile compound of exceptional reactivity. Malononitrile can be prepared in 80–96% yield by the reaction of cyanoacetamide and POCl₃ or PCl₅ in presence of inorganic salts.\(^1\)\(^-\)\(^2\) Due to the presence of active methylene protons, the reagent is found to be more useful in carbon–carbon bond formation reactions. It is used extensively\(^3\) as a reactant or reaction intermediate, since the methylene group and one or both cyano groups can take part in condensation reactions to give a variety of addition products and heterocyclic compounds. This unique reactivity makes malononitrile an important chemical in research and in medical, industrial and agricultural chemistry applications.

Abstracts

(A) A three-component reaction of sulfonium salt, malononitrile, and aldehyde in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF₆]), or in ethanol in the presence of triethyl amine, is a convenient one-pot method for the synthesis of substituted 1,1-dicyanocyclopropanes. This reaction involves stereoselectivity to form substituted trans cyclopropanes.\(^4\)

(B) A clean one-pot synthesis\(^5\) of tetrabenzo[b]pyran derivatives can be achieved from aromatic aldehyde, malononitrile and 5,5-dimethyl-1,3-cyclohexadione. The reaction uses hexadecyltrimethyl ammonium bromide (HTMAB) as a catalyst in aqueous media.

(C) Maggi et al.\(^6\) have reported an efficient and selective synthesis of substituted 2-amino-2-chromones by reaction of malononitrile, α-naphthol and aromatic aldehydes in water using basic alumina as heterogeneous and reusable catalyst.

(D) Malononitrile is an efficient reagent for the synthesis of 1,6-diketo compounds\(^7\) via a three-component Michael addition reaction. This reaction proceeds via initial condensation of an α-bromoketone with malononitrile to afford a β,β-dicyanoketone which undergoes in situ Michael addition reaction with α,β-unsaturated ketones.
(E) A new high-yielding multicomponent reaction providing multifunctionalized pyrido[2,3,d]pyrimidines has been accomplished in a microwave-assisted one-pot cyclocondensation of α,β-unsaturated esters, amidine systems and malononitrile.

(F) Condensation of carbonyl derivatives with active methylene compounds, such as malononitrile, is achieved within 3–15 minutes by a solvent-free reaction. Under microwave irradiation in the presence of carefully adjusted amounts of piperidine, Knoevenagel products are obtained in good to excellent yield.

(G) D-ring annelated pyridines are synthesized by the condensation of β-formyl enamides with cyanomethylenes such as malononitrile under microwave irradiation. This reaction has been successfully extended to acyclic and aromatic β-formyl enamides.

(H) A highly efficient palladium carbene complex catalytic system has been developed and successfully employed for cross-coupling of aryhalides with malononitrile anion.

References