

ABSTRACT

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Sophisticated synthesis in cyanochemistry

Cyanochemistry is big area of organic chemistry produces many products – nitriles, cyanohydrines, aminonitriles and many further products. We will report synthesis of cyanogen, pivaloylacetone nitrile and synthesis of β -ketonitriles via addition of hydrogen cyanide to vinylketones including synthesis of commercial unavailable vinylketones.

We report a new binary Cu(n)/Fe(m) supported catalytic system for a green and sustainable oxidation of hydrogen cyanide to cyanogen by hydrogen peroxide. The binary catalytic system Cu(n)/Fe(m), wherein n has the value of I or II, m is II or III, is supported on an acidic cation-exchanger resin. Oxidation process was carried out in a mixture of methanol-water. It was found that only two undesirable by-products, carbon dioxide CO₂ and elementary nitrogen are formed during an oxidation of hydrogen cyanide. Relationship among input parameters, i. e. character and amount of an applied resin, quantity and ratio of supported Fe/Cu catalyst, presence and character of a potential ligand, input rates of both reagents, reaction temperature, and output values, i. e. relative contents of the target cyanogen and undesirable CO₂, were studied by using of artificial neural networks (ANNs). The model for the characterization of relationship within the processing system was found and described. On the base of this model the optimal input parameters were found and the process was optimized. Predicted optimal conditions of synthesis were successfully verified in experiments. It was found that weakly acidic polyacrylate cation exchanger applied without presence of potential ligands is the most convenient resin for the supported catalysis.

Further, we will report effective synthesis of pivaloylacetone nitrile by nucleophilic substitution of chlorine in starting pivaloylchloride by cyanide ion. Amount of byproducts, which are produced due to basic and nucleophilic properties of cyanide ion, we decreased by usage catalytic amount of sodium iodide. Sodium iodide causes reaction via reactive intermediate – pivaloyliodide (Finkelstein method) – and this reaction route is faster and pure product is obtained in high yield.

Finally, synthesis of 1-acylcycloalkenes and corresponding nitriles by addition of hydrogen cyanide on activated double bond is last part of our research. These nitriles are raw materials for synthesis of methyl esters and lactones for fragrance and flavor industry. Synthesis of 1-acyl cycloalkanes was provided by using a few methods – addition of acylchloride to alkene catalyzed by aluminium chloride or by homogeneous catalyst type Simmons-Smith followed by elimination at basic conditions (*N,N*-dimethylaniline); reaction of cycloalkanones with Grignard reagent followed by Ruppe rearrangement at acid conditions. Addition of acylchlorides was optimized by usage of Ce (III) ion as catalyst. Products of addition were obtained in good yields. Michael addition of hydrogen cyanide on 1-acylcycloalkenes is provided at basic conditions. Yields of some derivatives are quite good.