International Journal of Research in Engineering and Science (IJRES)
ISSN (Online): 2320-9364, ISSN (Print): 2320-9356
www.ijres.org Volume 11 Issue 1 ǁ January 2023 ǁ PP. 111-112

Alum as a greener catalyst in Organic Synthesis

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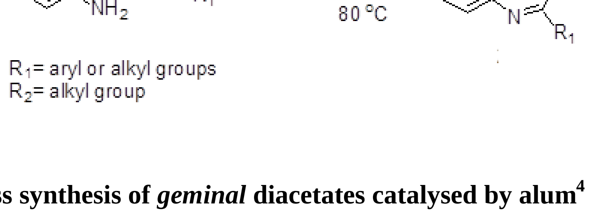
Abstract: *Green chemistry mainly focuses on reducing the impact of chemicals on human health and the environment. It emphasizes on the designing of chemical products and methodologies; minimizing the hazardous substances and maximizing the efficiency of chemical processes. The atom economy resulted in the usage of multicomponent reactions (MCRs). MCRs are convergent reactions, in which three or more starting materials react to form a product, where all or most of the atoms contribute to the newly formed product. The use of Lewis acids in organic synthesis is one of the most important fields in synthetic organic chemistry. The metal ions and their complexes are used in initiating and promoting varied types of organic reactions. Therefore, we felt that coupling metal ions with suitable adsorbent, by virtue of their synergistic catalytic activity, could prove efficacious in the synthesis of the target compounds. Furthermore, the use of reagents impregnated on inorganic supports offers various advantages such as simple work-up and product purification at the reaction completion, enhanced or reduced reactivity of the functional groups in the substrates, selectivity that may be different from that in solution and manipulative simplicity.*
Key words: *Green Chemistry, MCRs, Lewis acids, Alum*

Date of Submission: 01-01-2023 Date of acceptance: 08-01-2023

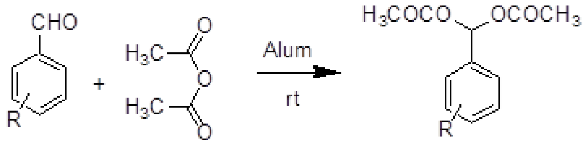
Alum: The salts of alkali metals react with equivalent quantity of sulfates of trivalent metals such as Fe, Al and Cr to form the soluble double salts referred to as alums. The alumsare crystalline in nature and are associated with twenty-four molecules of water of crystallization ($M_2^{I}SO_4M_2^{III}(SO_4)_3.24H_2O$). e.g., hydrated aluminum potassium sulfate $K_2\ SO_4Al_2(SO_4)_3{\cdot}24H_2O$ or alum also known as *phitkari* was used for the treatment of water by Indians for hundreds of years. Alum being inexpensive is used in dyeing, pulp and paper industry. Alum acts as a coagulant and therefore removes turbidity, suspended solids and colloidal colour, reduces biochemical oxygen demand and clarifies wastewater. Alum is also used as a base in skin whiteners and in block form as an aftershave. Alum powder is used as a preservative in pickling recipes to maintain crispness. It is also used in manufacture of zeolites and aluminosilicate catalysts. Alum[1] is also used as an efficient, non-toxic and cheap green catalyst in organic synthesis.Being safe, it is preferably used as a Lewis acid in research institutions and industry to avoid the use of toxic organic reagents. Alum[2]has been used in the synthesis of dihydropyrimidines and *cis*-isoquinolinic acids.

Synthesis of benzodiazepines using alum[3] under solvent-free conditions
Benzodiazepines are often used for short-term relief of severe, disabling anxiety or insomnia. Due to their biological importance synthesis is being carried out using various catalysts. Many of these methods involvethe use of strong acids, hazardous solvents, expensive reagents, high temperature conditions, extended reaction times, co-occurrence of several side reactions and use of stoichiometric amount of catalyst. Therefore, a need arises to develop an efficient and environmentally benign catalytic method for the synthesis of benzodiazepines by using inexpensive and non-polluting reagents. Keeping this in mind we envisioned the cyclocondensation of 1,2-diamines with ketonesin presence of non-toxic and cheap alum.



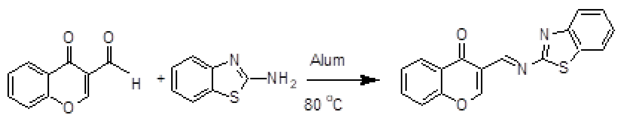
Chemo selective solvent-less synthesis of *geminal* diacetates catalysed by alum[4]
Non-toxic, cheap and environmentally benign alum $KAl(SO_4)_2{\cdot}12H_2O$ was utilized as an efficient green catalyst for the conversion of aldehydes into *gem*-diacetates or acylals**.** However, ketones did not form acylals;

giving rise to chemo selectivity.The *gem*-bisacyloxyalkanes or *geminal* diacetates or acylals[1] are stable to neutral and basic conditions[2] and can be easily converted back to parent aldehydes. This property of gemdiacetates i.e., stability towards a variety of reactions has been utilized in organic synthesis. Therefore, acylals are used as protecting groups for carbonyl compounds.



Alum[5]catalyzedsolvent-lesssynthesis of imines of 3-formylchromones

In our effort to develop imines as hybrid molecules, we conceived their synthesis from 3-formylchromone and 2-aminobenzothiazole in presence of alum as a green catalyst.Imines are biologically active and are known to possess antibacterial, antimicrobial,antifungal, antitumor, and herbicidal properties.3-Formylchromone derivatives have been extensively used as versatile building blocks for the synthesis of variety of heterocyclic systems.In our effort to develop hybrid molecules, we conceived the synthesis of imines from 3-formylchromone and 2-aminobenzothiazolein presence of alum as a green catalyst.



Solvent-less synthesis of Hybrid molecules of 3-formylchromonescatalyzed by alum[6]

In our effort to develop hybrid molecules, we conceived the synthesis of hydrazones from 3-formylchromone and carboxylic acid hydrazidesin presence of alum as a green catalyst, we conceived the synthesis of hydrazones from 3-formylchromone andcarboxylic acid hydrazides in presence of alum as a green catalyst in extension to our work.

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