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Original Article

USE OF ALUMINA IN PREPARATION OF OXIME: A PRECURSOR FOR BECKMANN REARRANGEMENT

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ABSTRACT

Objective: Oxime is an important precursor for many reactions like Beckmann rearrangement, oxime ether preparation etc. Oxime is generally prepared in strong acidic [1], strong basic [2] medium. Even some methods involving mild basic medium [3] is also known. But these procedures involve hazardous chemicals like inorganic acid, inorganic base, organic bases like Pyridine [4], Hy amine [5] etc. Some green methodologies have been also developed but that also involves expensive reagents like Bi_2O_3 [6] etc. In this context, this work has been carried out to develop a new methodology for oxime preparation.

Methods: Different oxims have been prepared in heating condition using water-ethanol medium and alumina as a base. Products have been isolated by column chromatography using 200 mesh silica gel followed by fractional crystallization. Products were verified by melting point analysis.

Results: Four different aromatic oxims have been prepared in excellent yield and in an economically viable condition.

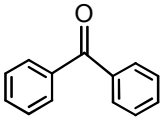
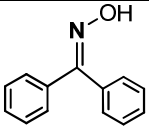
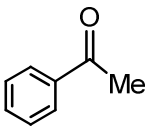
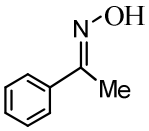
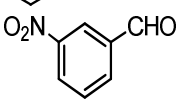
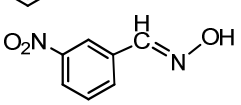
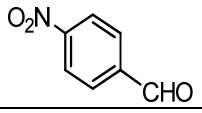
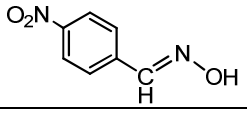
Conclusion: Here preparation of oxime in a mild basic medium has been reported. Alumina (Al_2O_3) is pretty cheap and not mentionable hazardous and it has been used here for the first time in synthesis of oxime.

Keywords: Alumina, Beckmann Rearrangement, Column Chromatography, Ethanol, Hydroxylamine Hydrochloride, Oxime, Thin Layer Chromatography.

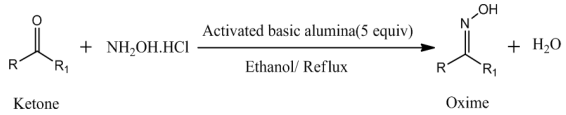
INRODUCTION

Classical method of oxime preparation involves strong basic or acidic medium. These strong conditions affect the selectivity of the process. Looking at the importance of oximes it is necessary to build up new methodologies of its preparation. Obviously appreciable methodology demands selectivity, lower expenditure, high yield, moderate conditions, easy isolation of the product and finally it needs to be a greenery approach towards the environment. Use of alumina as a reagent in preparation of oximes is an excellent choice in these points of view.

Oximes are the precursor for Beckmann rearrangement [7]. Beckmann reactions result "Lactum" and it is an important step for the synthesis of many biologically active as well as inactive molecules. Oximes can be used as an intermediate for preparing Nitriles [8], Nitrile oxides [9], Nitrones [10], Nitro compounds [11] etc. They are extensively used for the purification and characterization of carbonyl compounds [12]. Some oximes are very reactive; hence they can be used as inhibitors also [13]. Cyclohexanone oxime is extensively used in preparation of Nylon-6. That is why oximes have a big academic as well as industrial importance. As it is one of the major constituents in synthesis of many active drugs, it has a great demand in pharmaceutical industries also. Asoxime chloride, Pralidoxime Chloride (used in treatment of organophosphate poisoning), Oxime ethers (used as anti-inflammatory and antifungal substance), Methyl ethyl ketoxime (skin preventing additive), Beta-lactum (used as antibiotic), Acetaminophen (Used as analgesic and antipyretic) are few oxime derivatives which are very important in pharmaceutical industries.

Aldehyde/ketone	Oxime	Time (Hour)	Melting point		Yield (%)
			Lit.	Obs.	
		4	142	140	50
		3	59	57	80
		2	120	119	85
		2	132	130	88

A general method for the preparation of oximes can be illustrated in the following way: 1 gm of each sample was taken in a round bottomed flask and it was dissolved in minimum volume of ethanol then 1.5 equivalent of hydroxylamine hydrochloride was dissolved in minimum volume of water and it was poured in the round bottomed flask. Five equivalents of alumina were added to it and the mixture was refluxed. The reaction mixture was studied using Thin Layer Chromatography in a regular interval. Then the solvent was evaporated by rotavac and normal workup with ether gave the crude product. Oxime was separated from the reactant using an appropriate method of separation (like column chromatography or fractional crystalisation etc.) for individual cases. Recrystalisation was performed in aqueous ethanol.



Here Alumina acts as a Lewis base. It takes the proton from hydroxylamine hydrochloride and makes hydroxylamine free. Hydroxylamine attacks the carbonyl center of aldehyde/ketone, followed by water elimination it results the oxime. Ethyl alcohol is being a polar organic solvent it dissolves the ketone/aldehyde as well as the hydroxylamine hydrochloride. As the reactants are in the same phase, the reaction is expected to be associated with high yield. And it appears to be. Oxime is highly polar in nature. So it is soluble in ether. Alumina being a solid substance, it does not create any problem in separation. Benzophenone being a satirically hindered molecule its carbonyl carbon is difficult to be attacked. As a consequence it undergoes a low yield reaction. On the other hand presence of the nitro group in Para-nitro benzaldehyde increases the nucleophilicity of the carbonyl group. As a result it undergoes a high yield reaction.

CONCLUSION

Alumina being an amphoteric oxide it is pretty mild in nature, which is why it rarely involves unexpected reactions while it is used for oxime preparation. Being a cheap oxide it is useful in economic point of view also. Alumina being solid can easily be removed just by filtration with cotton to get the desired product. From the above table, it is very clear that the methodology is associated with high yield involving no mentionable pollutant and it has been achieved just by using a very cheap amphoteric oxide.

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CONFLICT OF INTERESTS

Declared None

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