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AN EFFICIENT ONE-POT SYNTHESIS OF AROMATIC NITRILES FROM ALDEHYDES USING Fe MODIFIED K10.

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Abstract: Aromatic aldehydes were converted to the corresponding aromatic nitriles in one step using hydroxylamine hydrochloride and FeCl₃ modified Montmorillonite K10.

The conversion of aldehydes to nitriles is an important chemical transformation¹. The most popular route for the transformation is: aldehydes converted to their oximes and then dehydrated to the nitriles. Dehydrating agents like selenium dioxide in chloroform², Chlorosulphonyl isocyanate³, 4,6-diphenyl-2-methylthio-pyrilium tetrafluoroborate⁴, DCC in presence of CuCl₂⁵, triphenylphosphine carbon tetrachloride in acetonitrile⁶ have been employed for this step. There are other reports of direct conversion of aldehydes to nitriles by

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using reagents such as free sulphimide⁷, N-tosylimines⁸, S, S- dimethylsulphurdiimide⁹, trimethylsilyl azide¹⁰, triazidochlorosilane¹¹, O-(2-aminobenzoyl) hydroxyamine¹², hydroxyamine/phosphoric acid¹³, hydroxylamine hydrochloride/ formic acid¹⁴, hydroxylamine/selenium dioxide¹⁵, hydroxylamine in toluene in presence of pyridine¹⁶, hydroxylamine hydrochloride/ MgSO₄,/ ToSOH¹⁷, lead tetraacetate¹⁸; and the most recently reported method using hydroxylamine and phthalic anhydride¹⁹, however, most of these methods require reagents that are corrosive, toxic, expensive, or are commercially unavailable. There have been attempts to heterogenise the reaction procedure by use of solid supports²⁰⁻²². However, in these cases, the reactions require high temperature or long reaction times²⁰, or preparation of oximes from aldehydes^{20,21} before dehydration.

We have earlier reported the use of FeCl₃ modified Montmorillonite K10 for Beckmann rearrangement²³ and Friedel-Crafts benzylation²⁴. During the study of substrates in the case of Beckmann rearrangement we found that when the clay used was less than the optimum quantity required for the transformation, or when the reaction was carried out at room temperature, the ketoximes underwent 'Beckmann fragmentation' to give benzonitrile. On this background we studied the reaction of aldoximes in the presence of Fe-modified K10 and found that it yielded nitriles as against anilides. Extending the reaction further, we found that when the reaction of aryl aldehydes with hydoxylamine hydrochloride was carried out in the presence of the catalyst, tandem oximation followed by dehydration took place to give nitriles directly with no sign of rearrangement. K10 was modified using FeCl₃ solution of acetonitrile, and activated at different temperatures²³. Best results were obtained using the clay activated at 280°C²⁸.

Scheme



Various aromatic aldehydes were studied for their conversion into the corresponding nitriles. The products were compared with the authentic samples.

General Procedure:

0.8 g of FeOO280, (The catalyst FeOO280 was prepared as per the reported procedure²⁴ and preserved in a desicator and activated overnight at 120°C, prior to use) is taken in a batch reactor and 10ml of toluene (dried over sodium) is added to it. Benzaldehyde (2mM) and 0.2 g of hydroxylamine hydrochloride is added to the reaction flask, the mixture is refluxed, with constant stirring. The water evolved in the reaction is removed azeotropically using a Dean-stark apparatus. The reaction mixture is filtered, toluene removed by distillation and the product is purified. The products were confirmed by recording their melting points and IR spectra.

Substrate	Reaction	Conversion	Selectivity	Selectivity for	Yiclds by
	time	of aldehyde	for nitrile	oxime	reported
					Methods
	(h)	(%)	(%)	(%)	(%)
Benzaldehyde	4	100	72ª	28	70(15) ²⁰
4-Chlorobenzaldehyde	4	100	95.8ª	4.2	8 6(13) ²⁰
3-Chlorobenzaldchyde	7	100	86 ⁶	14	77(8) ²⁵
4-Cyanobenzaldehyde	5	100	98 ^b	2	70(8) ²⁵
3-Bromobenzaldehyde	6	93	47ª	46	71(8) ²⁵
4-Hydroxybenzaldchyde	7	100	66"	34	91(7) ¹⁹
Salicyaldehyde	7	48.5	0*	48.5	
p-Anisaldehyde	6	100	94 °	6	92(7) ¹⁹
Vanillin	6	100	57 °	43	62(8) ²⁵

Table: Conversion of aldehydes to nitriles using hydroxylamine hydrochloride and FeOO280.

a: determined by GLC, b: Isolated yields The figures in the parentheses indicate the reaction time.

Vanillonitrile can be easily converted to vanillamine²⁶ by reduction, which on acylation gives "capsaisinoids". Salicaldehyde is known to form a complex with Fe^{43} , and thus we observed no dehydration of the oxime in this case, unlike 4-hydroxybenzaldehyde, where no such complexation is possible. Citral an aliphatic aldehyde on the other hand underwent Beckmann rearrangement to give an amide, similar to the diaryl ketoximes²³. Nitrobenzaldehyde does not undergo reaction by this procedure, probably due to the presence of a strongly electron withdrawing group. All the other aromatic aldehydes underwent dehydration to form nitriles in good yields.

The observations show that aromatic aldehydes can be easily converted to nitriles in high yields, and the reactions are clean. The reaction is an efficient onepot procedure with a simple work-up and where no expensive reagents are required.

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27. FeOO280 gave the maximum yield of 66.6% in two hours, whereas FeOO120 and FeOO550 gave 53.2% and 32.2% yield respectively.

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