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CALCINEÐ MgAICO₃-HT CATALYSED CYANOSILYLATION OF CARBONYL COMPOUNDS AND NUCLEOPHILIC RING OPENING OF OXIRANES USING TMSCN⁺

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ABSTRACT: Nucleophilic addition of TMSCN to carbonyl compounds is found to be catalysed efficiently using hydrotalcite as a solid base. The catalyst is also found to be active in the nucleophilic ring opening of oxiranes giving high regioselectivity.

Nucleophilic addition of TMSCN to carbonyl compounds has been a subject of extensive studies due to its usefulness in the synthesis of organic compounds such as cyanohydrins and β - amino alcohols. It is generally performed using various homogeneous catalysts such as ZnI₂, Lewis acids such as LaCl₃, AlCl₃, KCN.18-Crown-6, ⁿBu₄N⁺CN⁻ etc¹. Current trend is focused on the replacement of liquid catalysts with environmentally friendly solid ones. Hence

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various solid acids and bases such as Zeolites, Clay montmorillonite, Hydroxyapatite, Calcium fluoride etc. are increasingly finding application not only in TMSCN addition reactions but also in acid base catalysis². Besides providing operational simplicity, and higher selectivity with the scope for reusability, these solid catalysts have shown a synergistic reaction promoting effect due to the presence of both acid and basic sites on the surface of solid.

We have been investigating the utilities of mixed metal oxides obtained from hydrotalcite precursors for various organic transformations in liquid phase conditions³. The calcination of the mineral hydrotalcite⁴ -Mg₆Al₂(OH)₁₆CO₃.4H₂O (HT) which belongs to the anionic clay family leads to the formation of solid solutions of bimetallic oxides of the composition Mg₆Al₂O₈(OH)₂ which are homogeneously dispersed and are found to be highly basic in nature. Thus, the calcined hydrotalcite presents a unique class of heterogeneous catalysts which have pronounced but controlled basic character. The basic properties of hydrotalcites have been recognised for a long time, hence it finds use as an antacid. However, the catalytic application of hydrotalcite as a base has been limited to a few reactions in vapour phase conditions such as aldol condensations⁵ and polymerisations of olefin oxides⁶ etc.

We herein report the use of the basic mixed oxide obtained from hydrotalcite precursor for the cyanosilylation of carbonyl compounds giving almost quantitative yields of trimethylsiloxyalkanenitriles. Further, nucleophilic ring



opening of oxiranes using TMSCN induced by hydrotalcite catalyst as a solid base is also reported (Scheme 1).

Results and Discussion :- The calcined hydrotalcite catalyst is found to be a efficient solid base for the cyanosilylation of aldehydes, ketones and enones, giving excellent yields of the products (Table 1). The reaction is extremely fast and very mild in comparison with the other reported methodologies using solid bases.

In case of enones, there is predominantly 1,2-addition. By products resulting from 1,4- addition are not observed.

The calcined hydrotalcite is also found to be a efficient catalyst for the ring opening of epoxides. The attack of CN⁻ always occurred on the less substituted epoxy carbon giving 3-trimethylsiloxyalkanenitriles (Table 2).

The higher reactivity of TMSCN in presence of bases can be understood in terms of the strong affinities of the oxide ion of base and silicon resulting in the increase in coordination number of silicon from the normal value of 4 to 5 or 6

Entry	y Substrate	Product	Time/min.	Yield (%)
	0 8 - Č - R'	OTMS R - C - R'		
1.	R = Ph, $R' = Me$	" ĊN	5	97
2 .	$R = p - MeOC_6H_4$, $R' = Me$)į	*	95
3.	R=p-MeC ₆ H4 , R'=Me		e e	99
4.	R = Ph, $R' = Ph$	"	"	99
5.	R = (0)0, R' = Me	17	u	97
6.	R = Me, R'=n-C ₆ H ₁₃	11	H	99
7.	R = Ph , R'= H	17	rr	99
8.	$R = o - NO_2C_6H_4$, $R' = H$	17	*	90
9.	$R = o - MeOC_6H_4$, $R' = H$	4	ų	98
10.	$R = PhCH \pm CH$, $R' = H$	11	60	90
11.	R = Ph, $R' = PhCH = CH$	V	120	92
	0 U	OTMS		
12.	\bigcirc	() (N	5	95
13.	Ö	OTMS CN	r	99
14.	ٻُ		"	95
15.	С ^Р сн ₃	OTMS CN CH3	•	94
16.			30	98
17.	сн ₃ — С — сн ₂ -С – ос ₂ н ₅	CH3-C-CH2-C-OC2H5	3 00	90

Table.1. Cyanosilylation of carbonyl compounds using calcined MgA1CO3-HT

Entry	Substrate	Product	Time h	Yield (%)
1.	\bigcirc		0.5	70
2.			3	95
Э	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~		3	90
4	$\bigcirc \circ$		3	72
5	\bigcirc \checkmark		2	95

Table.2. Nucleophilic ring opening of epoxides using calcined MgAICO₃-HT

giving a penta or hexa coordinate silicon compounds⁷ These penta and hexa coordinate silicon compounds have higher reactivities than the ordinary tetracoordinate silicon compounds. In addition the basic sites of MgAlCO₃-HT coordinates with TMSCN to release cyanide ion. Further, the salient feature of the present calcined hydrotalcite catalyst is the memory effect which allows the reconstruction of the original hydrotalcite structure with liberated cyanide ion intercalation, on exposure or contact with solutions containing CN^- anions and thus, makes the reaction more facile. Hence, the catalyst can also be recycled.



The hydrotalcite catalyst is thus, shown to be an efficient solid base in liquid phase conditions. Further, the scope of the catalyst for other base catalysed reactions, in liquid phase conditions, is being explored.

Experimental

Preparation of MgAlCO₃-HT:-

The MgAlCO₃-HT was obtained by the procedure reported by Reichle et al^5 . The catalyst was calcined at 723 K for 1 hr.

General procedure for Cyanosilylation of carbonyl compounds and nucleophilic ring opening of epoxides using calcined MgAlCO₃-HT:-

A 100 ml two necked round bottomed flask equipped with a magnetic stir bar was charged with 200 mg of calcined MgAlCO₃-HT, the substrate (4 mmol) in dry heptane under N_2 atmosphere. Trimethylsilyl cyanide (6 mmol) was then, added to the reaction mixture and the contents allowed to stir at room temperature. The reaction was monitered by thin layer chromatography(TLC). After the completion of the reaction the catalyst was filtered and the filtrate distilled under reduced pressure. The products were analysed by ¹H NMR. The products were further hydrolysed and column chromatographed to afford the corresponding hydroxy compounds.

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