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Natural Kaolinitic Clay : A Remarkable Reusable Solid Catalyst for the Selective Functional Protection of Aldehydes and Ketones

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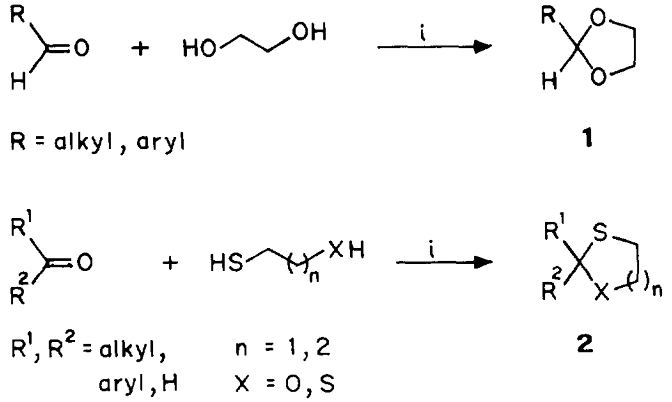
***Abstract** : Natural kaolinitic clay possessing transition metals such as Fe and Ti in its lattice has been found to catalyze efficiently the chemoselective acetalization and thioacetalization of variety of carbonyl compounds with ethane - 1,2 - diol and ethane - 1,2 - dithiol respectively.*

The carbonyl function, as present in aldehydes and ketones, is the most versatile functional group in organic synthesis. A major problem in a synthesis of any length is to shield a carbonyl function from nucleophilic attack until such time as its electrophilic properties must be exploited. One of the most useful protecting methods for carbonyl compounds is acetalization and thioacetalization.[1] Further, the use of dithiolanes and dithianes as blocking groups has raised a new strategy for electrophilic substitutions at the carbonyl carbon.[2] Recently, many catalytic systems such as $SOCl_2$-SiO_2[3], HY zeolite[4], Mg-ZnTf[5] and modified clays such as Mont-KSH[6] and Ce-Mont[7] have been developed for such synthetic transformations. However, the use of a reusable, heterogeneous catalyst such as natural clay, capable of achieving chemoselective protection of carbonyl functions including hindered ketones, and without shifting of the double bond to the β, γ - position while protecting the α, β - unsaturated carbonyl compounds, is of great interest.

Clays have many advantages such as ease of handling, non-corrosiveness, low-cost and regeneration. Due to their Bronsted and Lewis acidities, clays, both in their natural and ion-exchanged forms, function as efficient catalysts for various organic transformations.[8] We have also recently reported the catalytic property of natural kaolinitic clay for the regioselective chlorination of arenes.[9] In this communication, we wish to report that the kaolinitic clay catalyzes efficiently the chemoselective protection of a variety of aldehydes and ketones with ethane - 1,2 - diol or ethane - 1,2 - dithiol producing 1,3 - dioxolane (**1**) or 1,2 - dithioxolane (**2**) derivative respectively (Scheme 1).

The kaolinitic clay was procured from the Padappakara mine of Quilon District, Kerala, India and it was subsequently purified and characterized[9] by FT IR, XRD, UV, ESR, SEM, EDX and chemical analysis by AAS. The composition of the clay has been determined by wet chemical analysis (in %) : $SiO_2 = 67.45$, $Al_2O_3 = 22.2$, $Fe_2O_3 = 6.1$, $TiO_2 = 3.45$ and $K = 0.8$.



Scheme 1 : i) Clay (10% wt), ΦH, reflux, 2h

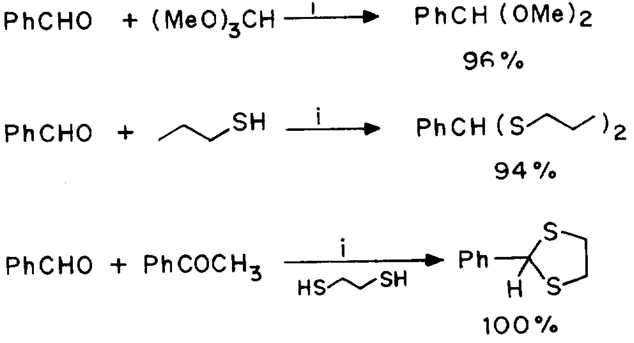
In a typical reaction procedure, a mixture of cinnamaldehyde (1.32 g, 10 mmol), ethane - 1,2 - diol (0.68 g, 11 mmol) and clay (132 mg, 10% mass) in benzene (25 ml) was refluxed for 2 h. After the reaction was complete (TLC), the clay catalyst was filtered off and the product purified by flash chromatography to afford 1,3 - dioxolane derivative (1.63 g, 93%, entry 17) as a colorless liquid.[10] The results are summarized in Table 1.

Table 1 : Protection of carbonyl functions with ethane - 1,2 - diol / dithiol catalyzed by kaolinitic clay

Entry	Substrate	1,3-Dioxolane **1** (%)[a]	1,3-Dithiolane **2** (%)[a]
1	1 - Butanal	91	92
2	1 - Hexanal	90	
3	Crotonaldehyde	92	
4	3-Methylcyclohex-2-en-1-one	0	90
5	(R) - Carvone	0	72
6	(R) - Camphor	0	85
7	Acetophenone	0	97
8	Benzaldehyde	95	98 (95)[b]
9	4 - Chlorobenzaldehyde	81	
10	4 - Methoxybenzaldehyde	92	
11	4 - Hydroxybenzaldehyde	40	85
12	4 - Nitrobenzaldehyde	75	
13	3,4,5 - Trimethoxybenzaldehyde	86	
14	1,4 - Benzenedicarboxaldehyde[c]	92	88 (94)[d]
15	Furan - 2 - carboxaldehyde	93	
16	Pyridine - 2 - carboxaldehyde	45	92
17	Cinnamaldehyde	93[e]	

a : Isolated yield, characterized by IR, ^{1}H and ^{13}C NMR and MS; b : Protected with 1,3 - propanedithiol (1,3 - dithiane); c : Underwent diprotection with 2 moles of reagent; d : Protected with 1,2 - ethaneoxathiol; e : Catalyst recovered and reused atleast 3 times without any loss of activity.

Evidently, the clay catalyzes the protection of a variety of aldehydes (aliphatic, aromatic, heteroaromatic, α, β - unsaturated) with ethane - 1,2 - diol. Ketones have, however, failed to undergo protection under such reaction conditions. In contrast, both aldehydes and ketones could be thioacetalized with ethane - 1,2 - dithiol producing 1,3 - dithiolanes in excellent yields. The protection of aldehydes were also achieved with 1,3-propane dithiol (entry 8) and 1,2 - ethaneoxathiol (entry 14). Even the sterically hindered ketones eg camphor could be easily thioacetalized with ethane - 1,2 - dithiol. A special feature of this catalytic process is that α, β - unsaturated ketones underwent protection without the shift of the double bond to β, γ - position (entries 4 & 5). In addition, benzaldehyde could also be acetalized with trimethyl orthoformate as well as 1-propanethiol in very high yield. In order to examine the selectivity of the present thioacetalization with use of the clay, an equimolar mixture of benzaldehyde, acetophenone, ethane - 1,2 - dithiol and 10% mass clay in benzene was refluxed for 2 h and it was found that perfect chemoselectivity was observed (Scheme 2).



Scheme 2 : i) Clay (10% wt), ΦH, reflux, 2h

The acid strength distribution of the clay (at 50°C, Bronsted acid sites = 21% and Lewis acid sites = 79%) was determined[9] by FT IR study of adsorbed pyridine. The enhanced catalytic activity of the acid activated clay could be attributed to the significant amount of Lewis acidity derived from Al remaining in the edges of the platelets and Bronsted acidity of coordinated hydroxy groups of Al^{3+}, Fe^{3+} and Ti^{4+} ions relocated in the interlamellar space of the clay.

In conclusion, the natural clay is an effective and convenient catalyst for acetalization and thioacetalization of carbonyl compounds and high chemoselectivity of the reaction should be useful for selective protection of aldehydes in the presence of keto carbonyl functions.

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10. All compounds exhibited satisfactory spectral data (IR, ^{1}H & ^{13}C NMR and MS).

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