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# $SiO_2$.CTB : Efficient Catalyst for Chemoselective Synthesis of 1,1-Diacetates and Benzimidazole under mild condition

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**Abstract:** Efficient method has been developed for the chemoselective Synthesis of 1,1-Diacetates and Benzimidazole using $SiO_2$.CTB under mild conditions. The remarkable selectivity, excellent yields, short reaction time, easily available and inexpensive catalyst, is important features of this method.

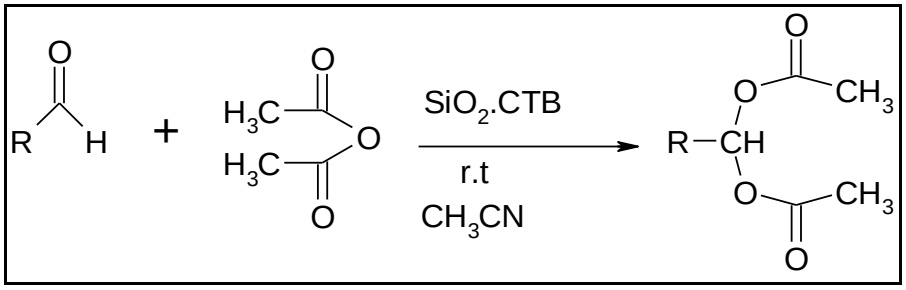
**Keywords** : chemoselective, 1,1-diacetates, $SiO_2$.CTB, aldehydes, acetic anhydrates, benzimidazole.

## Introduction

The development of simple, efficient, environmentally benign and economically viable chemical process or methodologies for widely used organic compounds are in great demand. Diacetylation reactions of aldehydes have received considerable attention in organic synthesis to develop a various useful organic compounds. Selective protection and deprotection of carbonyl groups are essential steps in modern organic chemistry.[1] Protective group acylals are fairly stable under neutral and basic conditions[1b] as well as under critically controlled acidic conditions. Apart from mere protective groups, acylals are important synthons and useful precursors. The 1,1-diacetates derived from α, β-unsaturated aldehydes are important starting materials in the Diels–Alder reaction[2]. These 1,1-diacetates have several synthetic and industrial applications and are used as cross-linking reagents[3] in cellulose and the cotton industry and are also used as stain-bleaching agents. As synthons, their usefulness has been exploited in well-known reactions of organic chemistry, such as the Grignard[4] , Barbier,[4b] and Prins[5] reactions, and condensation reactions, such as the Knoevenagel[6]and benzoins[7] reactions. Because of their unique properties as protective groups as well as important synthons, search for efficient, mild, and facile preparation of acylals is of current interest. Generally, acylals are prepared from aldehyde and acetic anhydride using strong protonic acids such as sulphuric, phosphoric, methanesulfonic or perchloric acids[8]. Use of strong Lewis acids[9] have also been reported. Apart from these catalysts, expensive[10] graphite, zeolite, tungstosilicic acid, and zirconium sulfophenyl phosphonate have also been employed in this protection process. Some of these methods still suffer from drawbacks such as prolonged reaction time(viz. up to 120 h in the case of 2-furyl aldehyde with $PCl_3$), low yields in the case of 4-nitrobenzaldehyde (4%) and cinnamaldehyde (30%) when $PCl_3$ is used, and in some cases the requirement of elevated temperature. Several of these catalysts are not very safe to handle, such as metal perchlorates and $BF_3$.

Consequently, it seems desirable and necessary to develop a simple, safe, efficient, and facile method for the preparation of these gemdiacetates. In this communication we wish to report $SiO_2$.CTB (silica supported coppertetrafloroborate) an efficient and very mild catalyst under mild conditions.

**Scheme 1.**

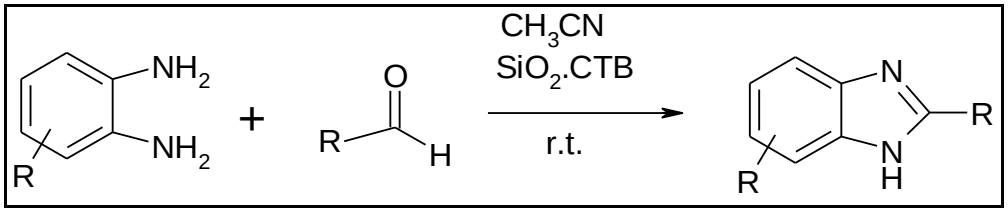



R: Alkyl, Phenyl

Benzimidazole are present in various bioactive compounds possessing antiviral, antihypertension and anticancer properties[11,12]. Compounds possessing the benzimidazole moiety express significant activity against several viruses such as HIV[13], Herpes(HSV-1) [14] and influenza[15]. Bis-benzimidazole is DNA-minor grove binding agents possessing anti-tumour activity [16].

The condensation of o-phenylenediamine with carbonyl compounds in the presence of strong acids such as polyphosphoric acid or mineral acids[17] and other reagents such as $I_2/KI/K_2CO_3$[18], N-halosuccinamide (X=Cl, Br, I)[19], $Yb(OTf)_3$ [20], PEG-100 [21], $(NH_4)H_2PW_{12}O_{40}$ [22] and palladium as well as microwave irradiation [23] and solid phase reactions [24] are reported in literature. However, many of the synthetic protocols reported so far suffer from disadvantages, such as a requirement for anhydrous conditions, use of organic solvents, harsh reaction conditions, prolonged reaction times, expensive reagents and low to moderate yields. Almost all the reported methods make use of an acid catalyst, giving rise to tedious working procedures. Therefore, the development of a cost-effective, safe and environmentally friendly reagent is still needed.

**Scheme – 2**




R: Phenyl, Alkyl

## Results and Discussion

In order to find out the most effective 1,1- diacetylation, benzaldehyde was chosen as a model substrate. It was treated with 2 equiv. of acetic anhydride in the presence of 1.0 mmol of $SiO_2$.CTB in different dry solvents and catalytic amounts at room temperature (Table 1). The reaction in THF, $CH_2Cl_2$, $CHCI_3$ , $Et_2O$, EtOAc, DMF (Table- 1 , entries –1-8) were found less effective. Since we have carried out the reaction using $CH_3CN$ to get the excellent yield (98%, entries-9, 10)

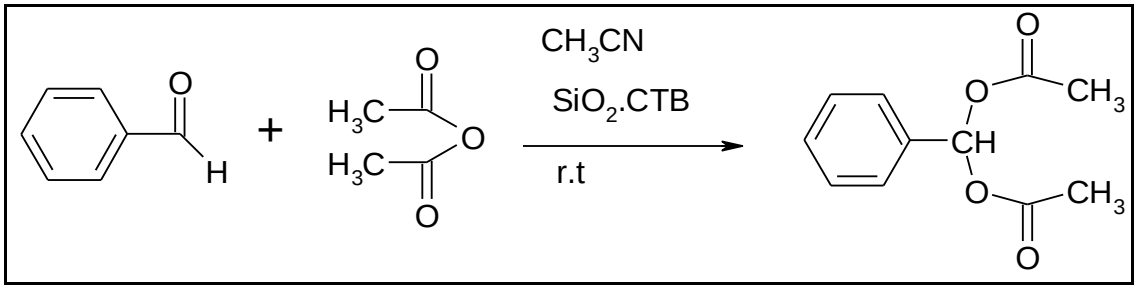


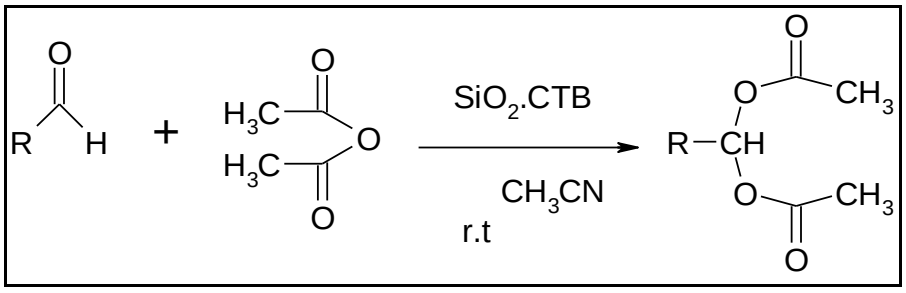
**Table- 1. 1,1- Diacetylation of benzaldehyde with acetic anhydried in the presence of $SiO_2$.CTB at room temperature with different solvents and catalytic amounts.**

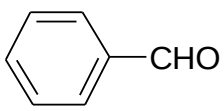
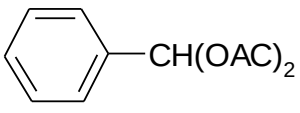
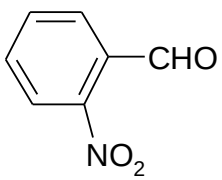
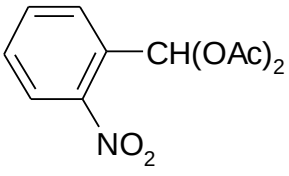
| Entry | $SiO_2$.CTB mmol | Solvent | Time(min) | Yield[a] ( %) |
|---|---|---|---|---|
| 1. | 1.0 | THF | 40 | 67 |
| 2. | 1.0 | $CH_2Cl_2$ | 40 | 86 |
| 3. | 1.0 | $CHCl_3$ | 40 | 76 |
| 4. | 1.0 | $Et_2O$ | 40 | 80 |
| 5. | 1.0 | EtOAc | 40 | 78 |
| 6. | 1.0 | DMF | 40 | 82 |
| 7. | 0.01 | $CH_3CN$ | 20 | 60 |
| 8. | 0.05 | $CH_3CN$ | 20 | 70 |
| 9. | 1.0 | $CH_3CN$ | 20 | 98 |
| 10. | 0.1 | $CH_3CN$ | 20 | 98 |

[a]Isolated Yield.

A variety of aromatic, aliphatic, and heterocyclic aldehydes were converted to corresponding 1,1-diacetates using acetic anhydride in the presence of $SiO_2$.CTB with excellent yields at room temperature and in short reaction times. The results are summarized in Table-2. All aromatic aldehydes carring electron donating or withdrawing substituents reacted well and gave excellent yields (Table 2, 1-14, 20-25). Aliphatics and α, β-unsaturated aldehydes produced acylals in good yields (Table 2, 16-19). Furfural is converted to its 1,1-diacetate in moderate yield (Table 2, entry -15). 4-(N,N- dimethylamineo) benzaldehyde gave less yield under the same condition of which may be due to electron donation of the dimethylamino group (Table 2, entry-25). We also studied the aldehydes having phenolic OH and carbonyl aldehyde groups under the above condition. We observed that both carbonyl and phenolic OH groups were acylated with corresponding yields (Table 2, entries-20-23). This reaction was further extended to aromatic compounds having two aldehyde groups were also acylated with respective yield (Table 2, entry-24).

**Table- 2. $SiO_2$.CTB catalyzed 1, 1- diacetylation of benzaldehyde**




| | Substrates | Products (b) | Time (min) | yield[a] (%) |
|---|---|---|---|---|
| 1. |  |  | 20 | 98 |
| 2. |  |  | 20 | 95 |

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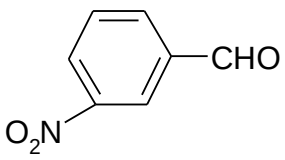
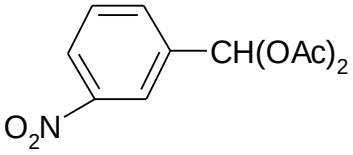
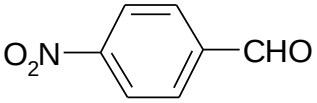
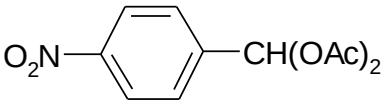
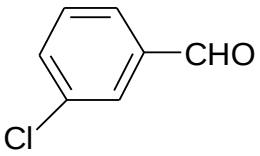
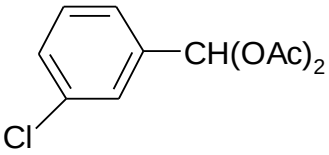
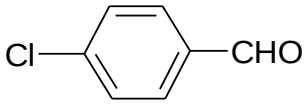
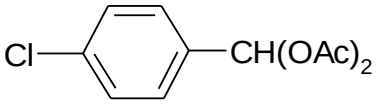
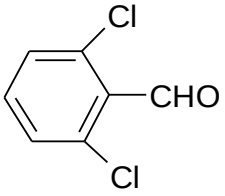
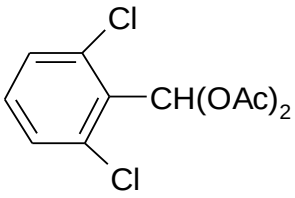
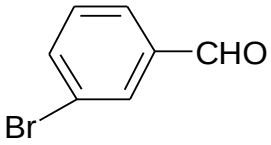
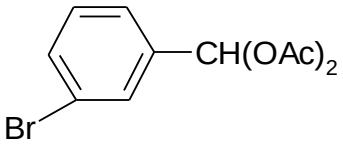
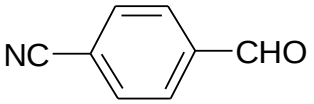
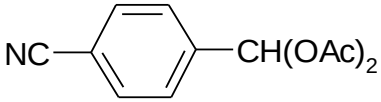
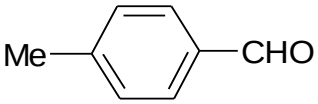
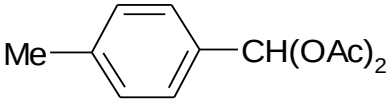
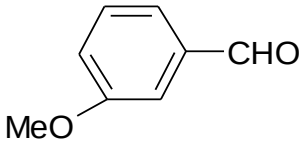
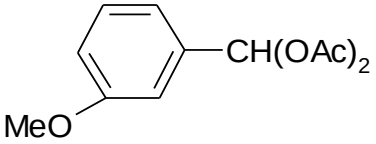
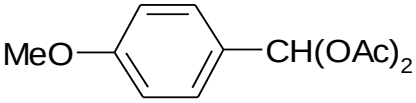
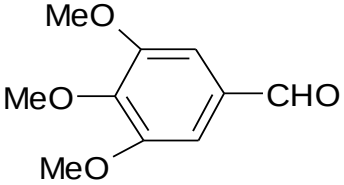
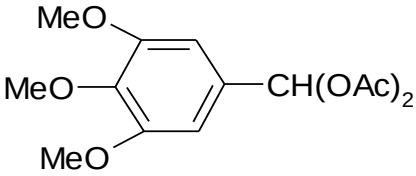
| 3. |  |  | 20 | 95 |
| 4. |  |  | 20 | 98 |
| 5. |  |  | 25 | 95 |
| 6. |  |  | 25 | 94 |
| 7. |  |  | 25 | 88 |
| 8. |  |  | 25 | 91 |
| 9. |  |  | 15 | 94 |
| 10. |  |  | 30 | 91 |
| 11. |  |  | 25 | 94 |
| 12. |  |  | 35 | 82 |
| 13. |  |  | 40 | 80 |

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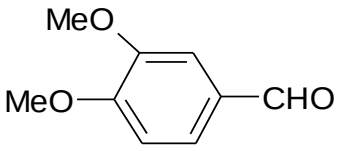
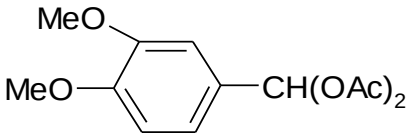
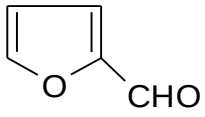
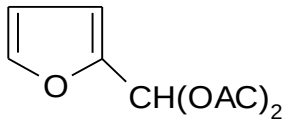
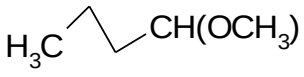
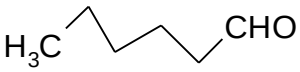
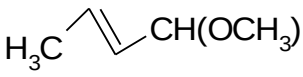
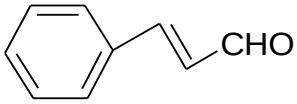
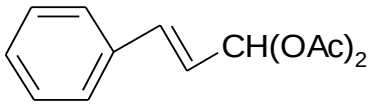
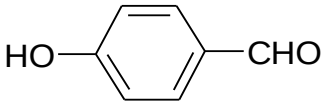
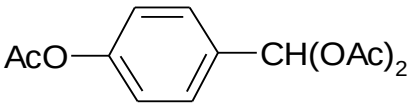
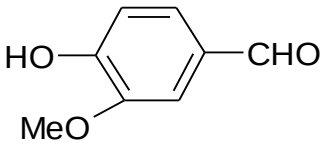
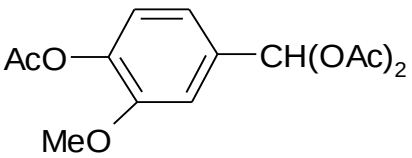
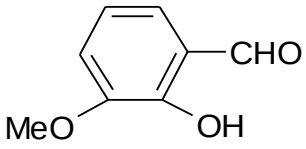
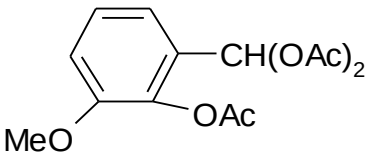
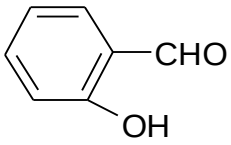
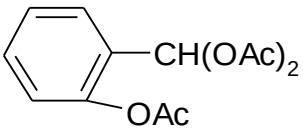
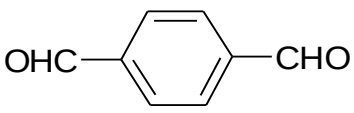
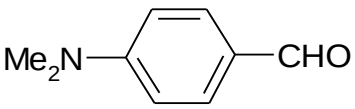
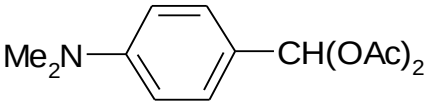
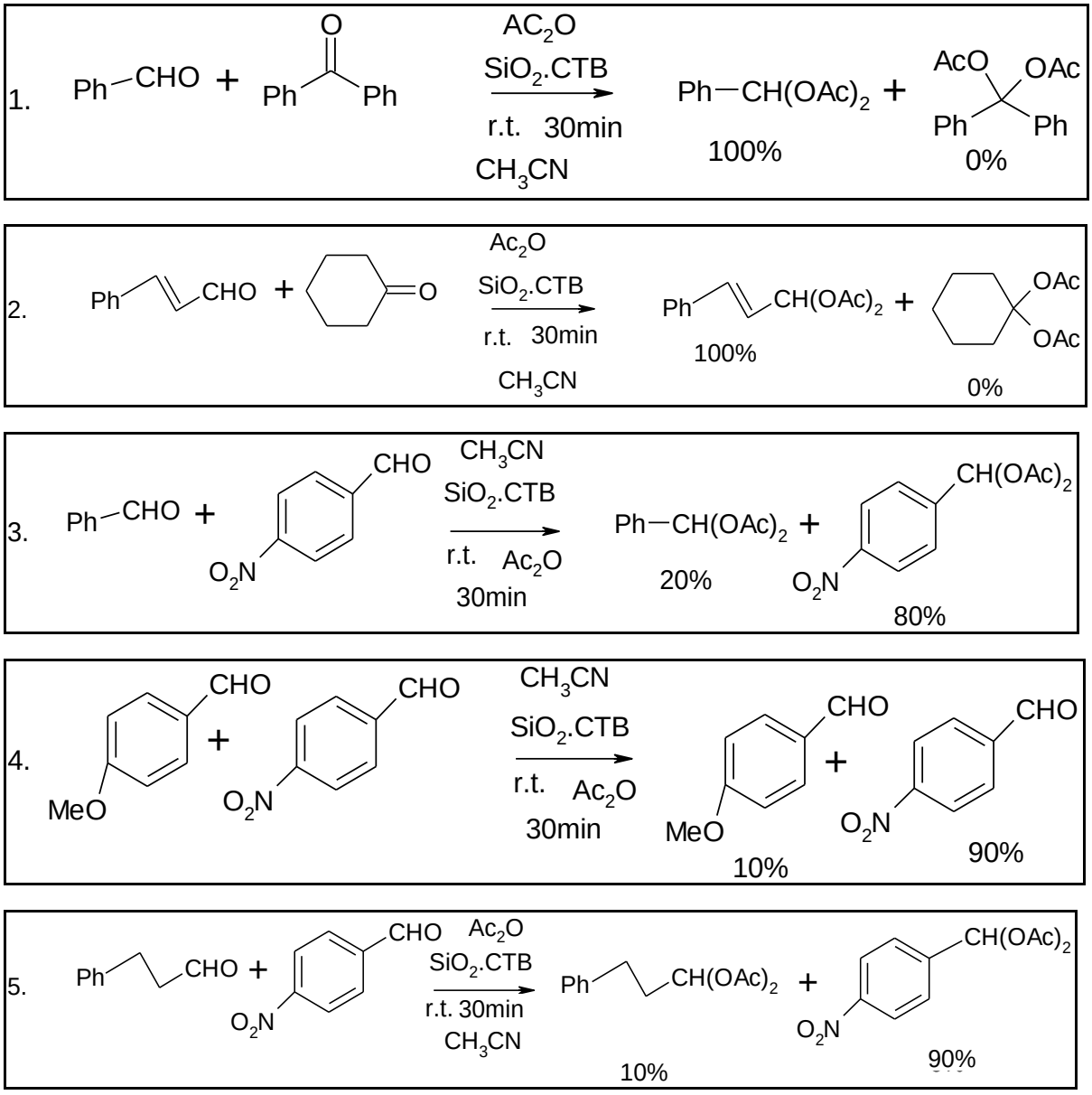
| 14. |  |  | 45 | 81 |
| 15. |  |  | 50 | 70 |
| 16. |  |  | 25 | 90 |
| 17. |  |  | 25 | 91 |
| 18. |  |  | 25 | 91 |
| 19. |  |  | 25 | 92 |
| 20. |  |  | 25 | 92 |
| 21. |  |  | 45 | 87 |
| 22. |  |  | 30 | 92 |
| 23. |  |  | 25 | 91 |
| 24. |  |  | 20 | 94 |
| 25. |  |  | 60 | 42 |

[a] Yields refer to pure products and all products were characterized by comparison of their IR, [1]HNMR spectra

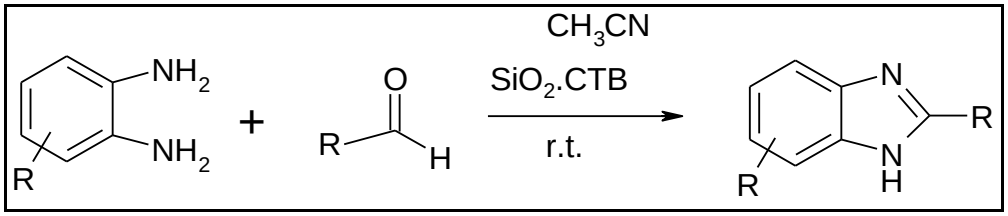
To evaluate the selectivity of this method, we investigated competitive reactions for aldehydes in the presence of ketones using $SiO_2$.CTB as catalyst under mild conditions. Employing this catalytic system, the highly selective conversion of aldehydes in the presence of ketones was observed (Table 4, entries-1-2). We also compared the acetylation of 4-nitro benzaldehyde versus benzaldehyde and 4-methoxy benzaldehyde. These reactions proceeded with high selectivity in the presence of this catalyst showing the importance of electronic effects upon these reactions in the presence of this catalyst (Table 3, entry-3,4). We also studied the

acylation of 4-nitrobenzaldehyde in the presence of 3-phenyl propionaldehyde under the same conditions. As shown in Table 4,(entry-5), the rate of acylal formation of 3-phenyl propionaldehyde is lower than 4-nitrobenzaldehyde which which may be due to enol formation of 3-phenyl propionaldehyde in the presence of this catalyst

**Table 3. Chemoselective Synthesis of Acylas from Aldehydes using acetic anhydride in the presence of $SiO_2$.CTB at room temperature**



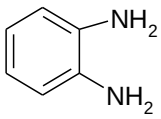
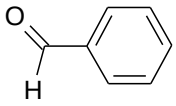
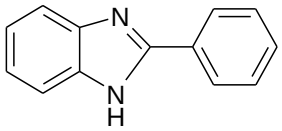
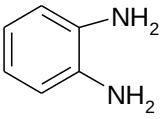
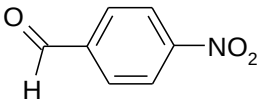
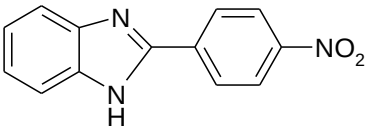
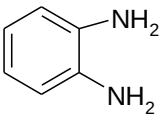
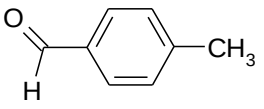
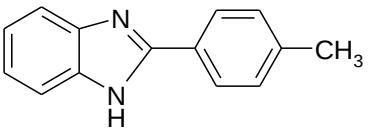
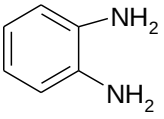
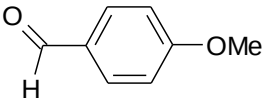
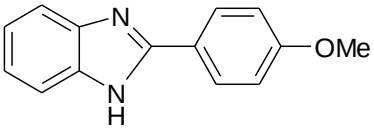
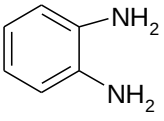
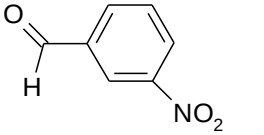
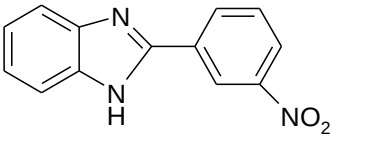
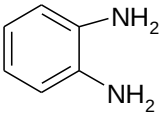
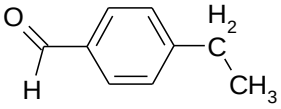
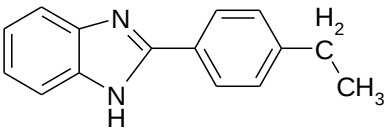
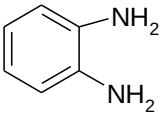
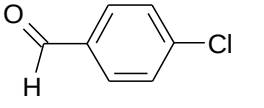
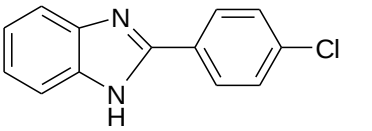
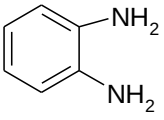
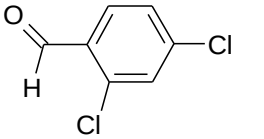
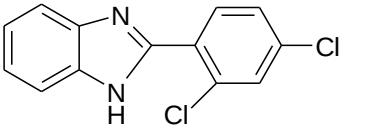
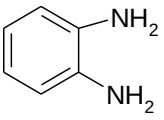
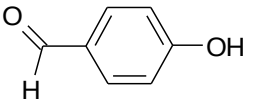
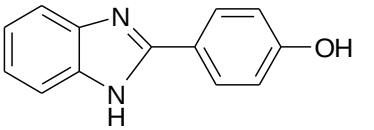
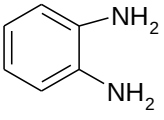
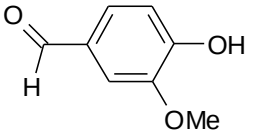
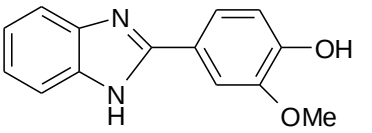

In this communication, we report a simple and efficient method for synthesis of benzimidazole derivatives using silica supported CTB as a catalyst under mild conditions.




R: Phenyl, Alkyl

A wide variety of compounds were applied under optimal reaction conditions to prepare benzimidazoles. The results are summarized in Table-3. Variety of aldehydes, aliphatic, heterocyclic and aromatic possessing both electron- donating and electrone withdrawing groups were employed for benzimidazole formation and in all cases, the yields were excellent. (Table-3, entries 1-18). Four different types of o-phenylenediamines were employed and all of them reacted smoothly under the reaction conditions. The aliphatic aldehydes which were also reacted under similar conditions gave considerable yields (Table-3, entries 12-13).

**Table- 4. Synthesis of benzimidazole in presence of $SiO_2$.CTB at room temperature**

| Entry | 1,2-Diamine[a] | Aldehyde | Product[b] | Time(min) | Yield[c] (%) |
|---|---|---|---|---|---|
| 1. |  |  |  | 10min | 94 |
| 2. |  |  |  | 10min | 95 |
| 3. |  |  |  | 10min | 92 |
| 4. |  |  |  | 15min | 90 |
| 5. |  |  |  | 20min | 91 |
| 6. |  |  |  | 15min | 94 |
| 7. |  |  |  | 10min | 90 |
| 8. |  |  |  | 20min | 91 |
| 9. |  |  |  | 25min | 87 |
| 10. |  |  |  | 40min | 87 |

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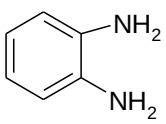
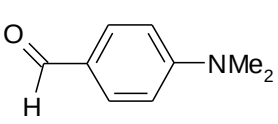
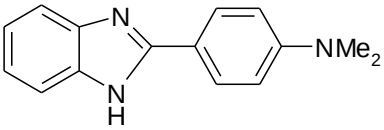
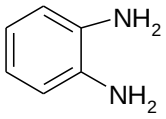
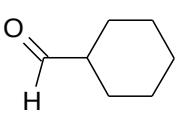
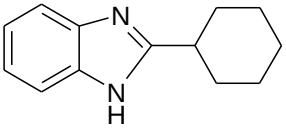
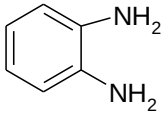
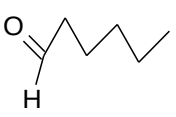
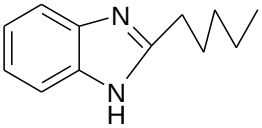
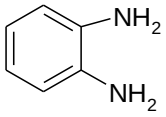
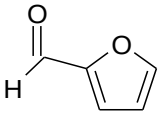
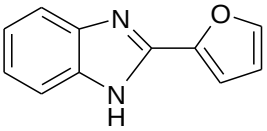
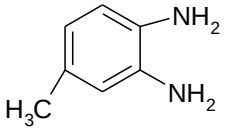
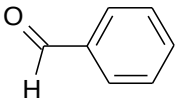
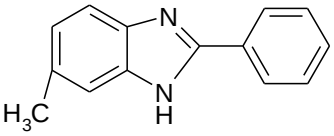
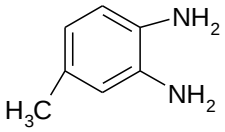
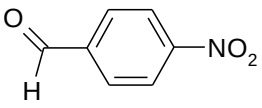
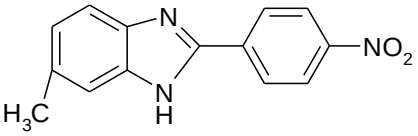
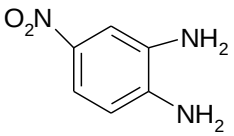
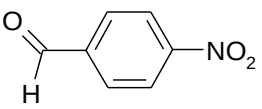
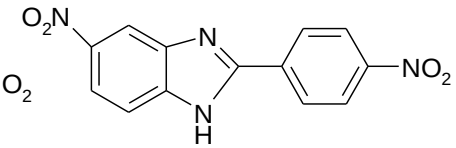
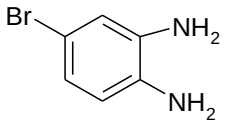
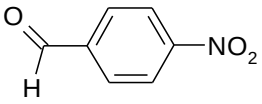
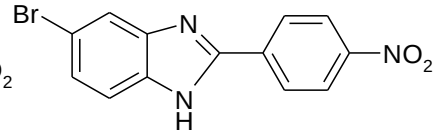
| 11. |  |  |  | 40min | 92 |
| 12. |  |  |  | 40min | 86 |
| 13. |  |  |  | 50min | 87 |
| 14. |  |  |  | 50min | 89 |
| 15. |  |  |  | 10min | 95 |
| 16. |  |  |  | 10min | 92 |
| 17. |  |  |  | 10min | 96 |
| 18. |  |  |  | 20min | 93 |

[a] The substrate was treated with benzaldehyde (2 mmol) by using $SiO_2$.CTB in solvent free conditions and at room temperature.
[b] All products were identified by their IR and $^1H$ NMR spectra
[c] Isolated yields.

**1. General Procedure for synthesis of 1,1-Diacetates derivatives:**

A mixture of aldehydes (2mmol), 5mmol acetic anhydride ($Ac_2O$) and 0.1mmol [CTB. $SiO_2$] was stirred magnetically at room temperature under mild conditions. While synthesis of benzimidazole derivatives were prepared by using mixture of o-phenyldiamine (2mmol), p-nitrobenzaldehyde (2mmol) and 0.1mmol [CTB. $SiO_2$] was stirred magnetically at room temperature with acteonitrile as a solvent and the progress of both the reaction was monitored by thin-layer chromatography (TLC).

In both the reaction, the mixtures were diluted with water (30ml) and extracted with chloroform (3x30ml). The chloroform extracts were dried with $Na_2SO_4$ and further purified by column chromatography and extracts concentrated under reduced pressure. In all the cases, the product obtained after the usual work up gave satisfactory spectral data.

**Characterization Data For Products:**

**a) 1,1-diacetates using $SiO_2$.CTB**

1,1-Diacetoxy-1-phenyl methane (1b):
IR (KBr): 3041, 1758, 1590,1515, 1458, 1368, 1244, 1200, 1058, 1015, 918, 842, 768, 690 $cm^{-1}$
$^1H$ NMR (300 MHz, CDCl3): δ = 7.6 (s, 1H), 7.32-7.49 (m, 5H), 2.0(s, 6H)
1,1-Diacetoxy-1-(4-nitrophenyl) Methane (4b):
IR (KBr): 3092, 1760, 1615,1525, 1355, 1229, 1210, 1066, 1012, 975, 857 $cm^{-1}$
$^1H$ NMR (300 MHz, CDCl3): δ = 8.24 (d, J = 8.4 Hz, 2H), 7.6 (d, J = 8.4 Hz, 2H), 7.23(s, 1H), 2.14(s, 6H)

**b) benzimidazole using $SiO_2$.CTB**

**( Table- 4, Entry 2):** IR ( KBr): 839, 1341, 1526, 1620, 2986, 3473 $cm^{-1}$

$H^1$NMR (300MHz, $CDCl_3$): δ = 6.8 (m, 2H, J=7.2Hz), 7.4 (d, 2H, J=7.2Hz) ; 8.1(d, 2H, J=7.2Hz); 8.3((d, 2H, J=7.8Hz); 8.5 (s, br, 1H, NH)

**( Table- 4, Entry 4):** IR ( KBr): 834, 1033, 1122, 1344, 1535, 1629, 2989, 3479 $cm^{-1}$

$H^1$NMR (300MHz, DMSO): δ = 3.23 (s, 3H), 7.53( s, broad, 2H), 7.67 (d, 2H, J=7.6Hz, 2H) ; 7.92 (m, 2H); 8.11(d, J=7.6Hz, 2H); 11.91 (s, 1H)

**( Table- 4, Entry 5):** IR ( KBr): 836, 924, 1044, 1108, 1128, 1356, 1545, 1628, 2989, 3479 $cm^{-1}$

$H^1$NMR (300MHz, DMSO): δ = 7.1( m, 2H), 7.54 (d, broad, J=7.5Hz, 1H) ; 7.63 (d, broad, J= 7.5Hz, 1H); 8.20(d, J= 6.8Hz, 1H); 8.54(d, J= 7.8Hz, 1H); 9.11 (s, 1H), 12.5 (s, 1H)

**( Table- 4, Entry 9):** IR ( KBr): 733, 814, 1037, 1538, 1628, 2928, 3328, 3477 $cm^{-1}$

$H^1$NMR (300MHz, DMSO): δ = 5.3 (s, 1H), 7.4( s, broad, 2H), 7.6 (d, 2H, J=7.6Hz, 2H) ; 7.9 (m, 2H); 8.1(d, J=7.6Hz, 2H); 12.2 (s, 1H)

## Conclusions:

In conclusion, this manuscript describes a method in which ($SiO_2$.CTB) is highly efficient catalyst for the diacetylation of aldehydes and synthesis of benzimidazole. The advantages include the low cost, ease of catalyst handling, very small amount of catalyst, mild reaction condition.

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