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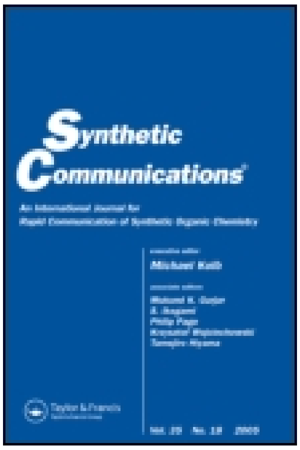

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SELECTIVE ACETYLATION OF ALIPHATIC HYDROXYL GROUP IN THE PRESENCE OF PHENOLIC HYDROXYL GROUP USING SILICA GEL SUPPORTED BF_3 CATALYST

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SELECTIVE ACETYLATION OF ALIPHATIC HYDROXYL GROUP IN THE PRESENCE OF PHENOLIC HYDROXYL GROUP USING SILICA GEL SUPPORTED BF_3 CATALYST

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Chemical Technology, Hyderabad, 500 007, India

ABSTRACT

Selective acetylation of aliphatic hydroxyl group in the presence of phenolic hydroxyl group was achieved conveniently and efficiently by treatment with EtOAc in the presence of silica gel supported BF_3 catalyst.

Selective acetylation of aliphatic hydroxyl group in the presence of phenolic hydroxyl group is an useful procedure in synthetic organic chemistry.[2] Such conversion has recently been carried out[2] by applying the process of transesterification using EtOAc in the presence of heterogenous catalyst, silica gel supported $NaHSO_4$. The catalyst is reported to work under heating condition.

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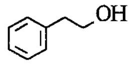
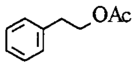
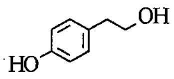
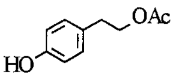
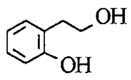
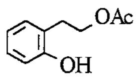
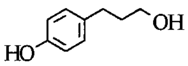
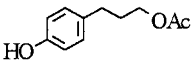
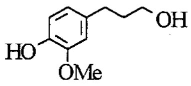
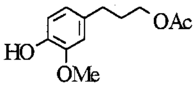
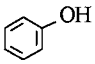
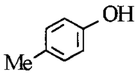
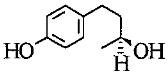
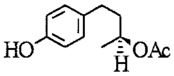
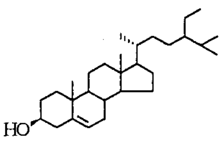
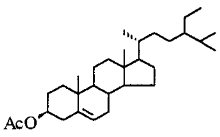
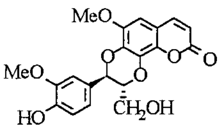
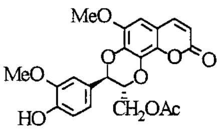
*Corresponding author.

Table 1. Selective Acetylation of Aliphatic Hydroxyl Groups†

Entry	Substrate	Product	Time (hr)	Isolated Yield (%)	Ref.
1			8	86	7
2			9	81	2
3			9.5	84	2
4			9	82	6
5			9	80	6
6		No conversion	10	--	
7		No conversion	10.5	--	
8			10	8	8
9			10.5	4	9
10			9.5	78	5

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† All the products were characterized from their analytical data and spectral (^{1}H NMR and MS) properties.

In continuation of our recent studies[3] on important methodologies useful for synthesis of bioactive compounds and their intermediates we have applied silica gel supported BF_3 catalyst at room temperature for selective acetylation of aliphatic hydroxyl groups. BF_3 is a versatile Lewis acid catalyst frequently used in organic synthesis.[4] Recently the silica gel supported BF_3 system has bee reported.[4] This heterogenous catalyst can easily be recovered and also minimise the production of waste formed during BF_3 recovery. However, the catalytic activity of the system has not yet been properly explored. We have observed that the system can efficiently be utilized for selective acetylation of aliphatic hydroxyl group in the presence of aromatic hydroxyl group. Previously BF_3 has not been reported to be employed for selective acetylation.

Different aliphatic alcohols have now been converted to the corresponding acetates by treatment with EtOAc in the presence of silica gel supported BF_3 catalyst at the room temperature (Table 1). Phenolic hydroxyl groups were uneffected under similar reaction conditions. The conversion of primary hydroxyl groups was achieved with very high yields (78–86%) but the compounds with secondary hydroxyl group afforded the desired acetates in poor yields (4–8%) along with some side products. The catalyst has effectively been utilized for the conversion of the natural antitumour coumarino-lignoid, cleomiscosin A into its analogue, venkatasin[5] (Entry no. 10). The structures of all the reaction products were settled from their analytical and spectral data.[6] Unsupported BF_3 decreased the yields of the products; primary alcohols produced the acetates with an yield of 37–45%.

In conclusion, a simple, mild and efficient method has been developed for selective acetylation of aliphatic hydroxyl group in the presence of phenolic hydroxyl group. The primary hydroxyl groups showed much higher reactivity compared to the secondary hydroxyl groups towards acetylation under similar reaction conditions. The common solvent EtOAc has been utilized for acetylating agent. The catalyst (silica gel supported BF_3) which has been used here for the first time for such conversion can easily be prepared from the readily available materials and conveniently be handled. The catalyst can also be recovered from the reaction mixture through simple filteration. The experimental procedure is simple and the conversion occurs at room temperature.

General Procedure: *p*-Hydroxyphenylethanol (Entry 2, 69 mg, 0.5 mmole) was dissolved in EtOAc (20 ml). Silica gel supported BF_3 [100 mg, prepared by reported method[3] using $BF_3{\cdot}OEt_2$ and silica gel (finer than 200 mesh)] was added. The mixture was stirred at room temperature under N_2 atmosphere for 9 h and filtered. The filterate was concentrated and subjected to column chromatography over silica gel to afford *p*-hydroxyphenylethyl acetate (73 mg, 81.1%).

ACKNOWLEDGMENT

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6. The spectral and analytical data of the two unknown acetates (entry nos. 4 and 5) are given below.

   3-(4-Hydroxyphenyl)propyl Acetate: Viscous mass, ^{1}H NMR (CDCl$_3$) : δ 7.05 (2H, d, J = 8.0 Hz), 6.73 (2H, d, J = 8.0 Hz), 4.11 (2H, t, J = 7.0 Hz), 2.62 (2H, t, J = 7.0 Hz), 2.08 (3H, s), 1.08–0.88 (2H, m); MS: m/z 194 (M$^+$); Anal. calcd. for $C_{11}H_{14}O_3$: C, 68.04; H, 7.22. Found C, 68.12; H, 7.17.

   3-(3-Methoxy-4-hydroxyphenyl)-propyl Acetate: Viscous mass, ^{1}H NMR (CDCl$_3$) : δ 6.87 (1H, d, J = 8.0 Hz), 6.75–6.66 (2H, m), 4.13 (2H, t, J = 7.0 Hz), 3.90 (3H, s), 2.65 (2H, t, J = 7.0 Hz), 2.10 (3H, s), 1.05–0.90 (2H, m); MS: m/z 224 (M$^+$); Anal. calcd. for $C_{12}H_{16}O_4$: C, 64.29; H, 7.14. Found C, 64.21; H, 7.08.
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