

Selective transesterification of alcohols in the presence of amines and phenols catalyzed by KHSO_4

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Abstract: A very simple method has been developed for the acylation of alcohols with ethyl acetate through a KHSO_4 -catalyzed transesterification. Using this method acylation of alcohols in the presence of amines and phenols has been achieved with high selectivity. The acylated products were obtained in high yields.

Keywords: Transesterification; KHSO_4 ; Acylation of alcohols; Ethyl acetate

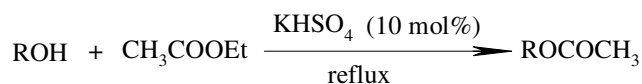
Introduction

Acetylation is one of the most applicable, beneficial and essential reaction in organic chemistry which has set chemists to introduce reagents for this reaction. Most procedures use acetic anhydride in the presence of acid or base catalysts [1]. Scandium(III) or Lanthanum(III) triflates were used as catalyst for the acetylation of alcohols with acetic acid [2], also $\text{La}(\text{OPri})_3$ [3], CoCl_2 [4] and $\text{Gd}(\text{OTf})_3$ [5] have been reported to promote the efficient acetylation of alcohols with acetic anhydride. The acetylation of alcohols with ethyl acetate and ethyl formate by $\text{Sn}(\text{OTf})_2$ [6], $\text{TiCl}_4/\text{AgClO}_4$ [7], $\text{AlPW}_{12}\text{O}_{40}$ [8] and Silphos [$\text{PCl}_3\text{-n}(\text{SiO}_2)_n$] [9] have also been reported. We have reported acetylation of alcohols and phenols with acetic acid or acetic anhydride in the presence of ferric perchlorate [10], $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ [11] and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ [12]. Very recently, we have also reported selective acetylation of alcohols and amines in the presence of a catalytic amount of heteropolyacid [13]. In continuation of our studies on the application of KHSO_4 as a green and reusable catalyst in organic synthesis [14,15,16], herein we introduce a simple and practical method for the selective acetylation of alcohols in the presence of amines and phenols using this catalyst (Scheme 1).

Results and Discussion

In fact, refluxing of 4-nitrobenzyl alcohol as a model

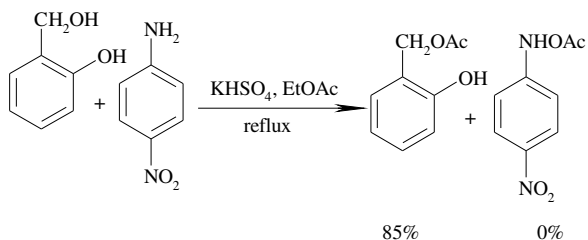
compound with excess of ethyl acetate afforded the benzyl acetate in 90% yield after 180 min. The product purity was established by IR. (Lack of the hydroxyl band: 3350 cm^{-1}) The IR spectra of the product showed strong absorption at 1736 cm^{-1} for the $\text{C}=\text{O}$ group. As shown in Table 1, a wide range of alcohols (Entries 1-7) underwent smooth acylation under the same reaction conditions whereas phenols (Entries 8-10) remained inert even after prolonged times. Thus selective acylation of an alcoholic OH group is achieved efficiently in compounds containing phenolic group in the same molecule (Entry 1). Like phenols, amines (Table 1, Entries 11-14) did not undergo any change by this procedure even after 24 h.



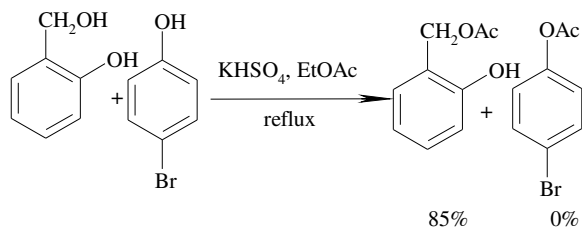
Scheme 1

Very interestingly, in a competitive acylation reaction with equimolar mixture of 2-hydroxy benzyl alcohol and 4-nitroaniline (Scheme 2) or 4-Bromophenol (Scheme 3) by this procedure, we found that the alcohol is acylated selectively in the presence of amine or phenol. The reaction is in general very clean giving high yields, and no by products has been isolated. The reactions proceeded well with 10 mol% of KHSO_4 and use of an increased amount of catalyst does not make much difference.

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Scheme 2



Scheme 3

Conclusion

In conclusion, we have demonstrated a very simple, efficient and clean protocol and practical method for the selective acylation of alcohols in the presence of a heterogeneous non-toxic, inexpensive and green catalyst

good to excellent yields. The significant features of this method include: (a) operational simplicity, (b) use of an inexpensive and non-toxic catalyst, (c) simplicity of work-up, and (d) high yield of products.

Experimental Section

All products were known and their physical and spectra data were compared with those of authentic samples. IR spectra were recorded as KBr disk on a FT-IR, Bruker Tensor 27. Mass spectra were determined on a Shimadzu QP-1100 EX spectrometer.

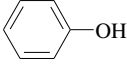

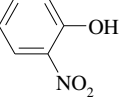
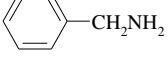
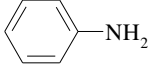
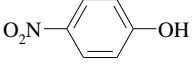
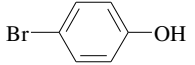
Acetylation of alcohols catalyzed by $KHSO_4$: Typical procedure

A solution of 4- NO_2 -benzyl alcohol (1mmol), $KHSO_4$ (10 mol %) and ethyl acetate (5mmol) was refluxed for 180 min. The progress was monitored by TLC (petroleum: ethyl acetate, 4:1). Upon completion of the reaction the catalyst was filtered off and washed successively with diethyl ether (10 mL). The mixture of organic solvents was washed with water and dried over $MgSO_4$. After evaporation of the solvent the pure product was obtained in 90% yield. The product was found to be pure by GC analysis.

Table 1. Acetylation of alcohols, phenols and amines catalyzed by $KHSO_4$

Entry	Substrate	Product	Time (min)	Yield (%) ^a
1			180	85
2			180	90
3			180	90
4			30	90
5			30	91
6			30	88

Table 1. Continued

8		No reaction	24h	-
9		No reaction	24h	-
10		No reaction	24h	-
11		No reaction	24h	-
12		No reaction	24h	-
13		No reaction	24h	-
14		No reaction	24h	-

^aYields refer to isolated products

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