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Convenient method for acetylation of alcohols with $[Cu_4(tu)_4Cl_4]$

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ABSTRACT

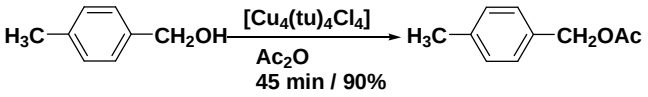
In this research transformation of alcohol to the corresponding acetates carried out using $[Cu_4(tu)_4Cl_4]$ at 50°C in acetic anhydrate without $NaBH_4$ in high to excellent yields.

KEYWORDS

Copper-thiourea complex;
Alcohols;
Acetic anhydrate.

INTRODUCTION

The conversion of alcohols to esters is an important synthetic transformation that has received considerable attention[1,2]. Conversion of an alcohol to the corresponding acetate is typically carried out using acetic anhydride or acetyl chloride in the presence of pyridine or triethylamine as a catalyst[3,4]. 4-(Dimethylamino)pyridine is known to cause a remarkable rate acceleration in the reaction[5]. In addition to catalysis by tertiaryamines, Lewis acids have also been reported to catalyze the acetylation of alcohols. Examples include TMSCl[6], $MgBr_2$[7], $Sc(AcO)_3$-$(CF_2SO_3)_2NH$[8], $TiCl^{4+}$, $AgClO_4$[9], $CoCl_2$[10], as well as $Sn(OTf)_2$, $Cu(OTf)_2$ and $In(OTf)_3$[11-13]. A highly efficient catalyst, $Sc(OTf)_3$, was introduced by Yamamoto[14]. However most of the reported methods suffer from one or more of the following disadvantages: long reaction time, vigorous reaction conditions, the occurrence of side reactions and unavailability of the reagents, as well as poor yields of the desired product. Thus, there is still a demand to develop new and mild methods for the acetylation of alcohols in the presence of in expensive and bench top reagents[15-17]. Transformation of alcohols to acetyl esters is one of the most important methods which has been received considerable attentions in organic synthesis specially in protection of functional groups. This goal was carried out in the presence of various reagents in acetic anhydride as a source of acetyl moiety[18,19]. Here in, we wish to report a clean, simple and efficient protocol for acetylation of alcohols using $[Cu_4(tu)_4Cl_4]$ in Ac_2O.



EXPERIMENTAL

All reagents and substrates were purchased from commercial sources with high quality and used without further purification. The products were characterized by their ^{1}HNMR or IR spectra and comparison with the authentic samples (melting or boiling points). Organic layers were dried with anhydrous sodium sulfate before concentration in vacuum. All yields referred to isolated pure products. TLC accomplished the purity determination of the substrates and products over silica gel GF_{254} aluminum sheets.

Preparation of catalyst $[Cu_4(tu)_4Cl_4]$

A hot solution of thiourea (0.89 g, 11.69 mmol) in ethanol (15 mL) was added into a hot solution of cop-

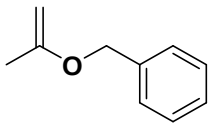
per chloride dihydrate (1.008 g, 5.91 mmol) in ethanol (I5 mL). The mixture was stirred and refluxed for 1h to give white solid suspension. The solution was filtered while hot and was allowed to cool to room temperature. The product was filtered, washed twice with ethanol and dried under vacuum. Yield 82.4%; m.p. 208.3-209.5 °C. IR (KBr)/cm^{-1} 3374(m), 328 I(s), 3 I74(vs), 2952(vs), 2853(sh), 1517(m), 1461 (m), 11100w), 721 (m), 473(m), 358(s)[22-25].

Reduction of alcohols to acetates with $[Cu_4(tu)_4Cl_4]$ in acetic anhydrate

In a round-bottom flask (10 mL) equipped with a magnetic stirrer, a mixture of benzyl alcohol (0.106 g, 1mmol) in Ac_2O(1.5 mL) was prepared. $[Cu_4(tu)_4Cl_4]$ (0.08mmol) was then added and the resulting mixture was stirred for 45 min in 50°C. TLC monitored the progress of the reaction (eluent: CCl_4/Et_2O, 5/2) was extracted with CH_2Cl_2 (3×5mL), dried over anhydrous Na_2SO_4. Evaporation of the solvent affords the pure benzyl acetate in 87% yield (TABLE 1, entry 1).

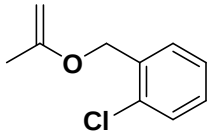
Selected data for benzyl acetate (1)

FT-IR (cm^{-1}): 3050, 2980, 1720, 1403, 1367, 1225, 1043, 755, 689. ^{1}H NMR (300 MHz, $CDCl_3$, δppm): δ2.18, 5.18, 7.42.^{13}C NMR (62.5 MHz, DMSO-d_6, δ ppm): δ 21.01, 65.32, 124.98, 127.66, 126.87, 139.43, 169.92.



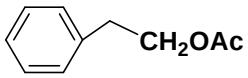
Selected data for 2-Chlorobenzyl acetate (2)

FT-IR (cm^{-1}): 3058, 2961, 1749, 1447, 1380, 1233, 1037, 757. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm): δ 2.15, 5.23, 7.37. ^{13}C NMR (62.5 MHz, DMSO-d6, δ ppm): δ 20.876, 64.638, 126.939, 128.246, 128.710, 129.563, 133.653, 170.695.



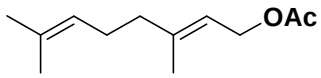
Selected data for 2-phenyl ethyl acetate (3)

FT-IR (cm^{-1}): 3063, 2957, 1739, 1496, 1454,1368, 1240, 1124, 1035, 748, 700, 641, 571. ^{1}H NMR (300 MHz, $CDCl_3$, δppm): δ2.013, 2.937, 4.341, 7.09 to 7.56. ^{13}C NMR (62.5 MHz, DMSO-d6, δ ppm): δ 21.92, 37.01, 66.89, 127.59, 129.76, 129.89, 138.67, 172.01.



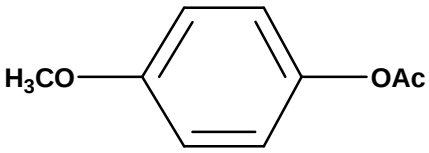
Selected data for geraniol acetate (4)

FT-IR (cm^{-1}): 2968, 2923, 1740, 1441, 1373, 1234, 1024, 956, 829,605,453. ^{1}H NMR (300 MHz, $CDCl_3$, δppm): δ 1.85, 1.98, 2.14, 2.52, 2.89, 4.98, 5.078. ^{13}C NMR (62.5 MHz, DMSO-d6, δ ppm): δ 17.65, 17.98, 21.05, 26.87, 27.77, 40.54, 62.69, 118.97, 125.29, 133.56, 142.97, 171.99.



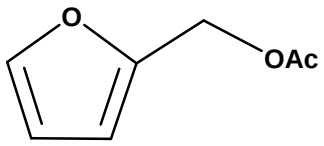
Selected data for 4-methoxy benzyl acetate (5)

FT-IR (cm^{-1}): 2967, 2845, 1742, 1618, 1521, 1242, 1177, 1031, 824. ^{1}H NMR (300 MHz, $CDCl_3$ δ ppm): δ 2.18, 3.93, 5.65 6.50, 7.65. ^{13}C NMR (62.5 MHz, DMSO-d6,δ ppm): δ 22.74, 57.17, 68.21, 123.94, 128.59, 132.79, 161.11, 172.52.



Selected data for furfuryl acetate (6)

FT-IR (cm^{-1}): 2971, 1742, 1625, 1503, 1434, 1373, 1237, 1152, 1021, 919, 817, 747. ^{1}H NMR (300 MHz, $CDCl_3$ δ ppm): δ 2.077, 5.69, 6.92, 7.03, 7.91. ^{13}C NMR (62.5 MHz, DMSO-d6,δ ppm): δ 22.65, 59.09, 111.71, 145.36, 150.72, 171.29.



RESULTS AND DISCUSSION

In course of our studies to explore more potentialities of $[Cu_4(tu)_4Cl_4]$ in organic synthesis, we found that acetylation of benzyl alcohol with $[Cu_4(tu)_4Cl_4]$ in ace-

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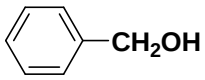
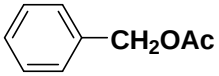
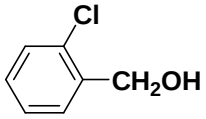
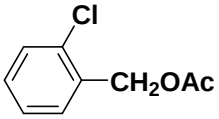
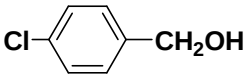
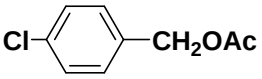
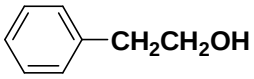
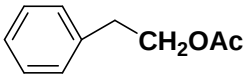
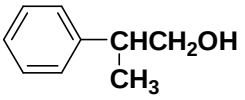
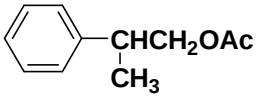
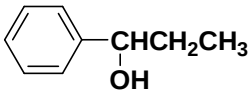
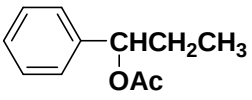
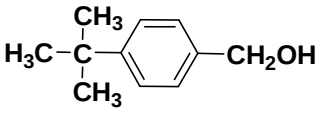
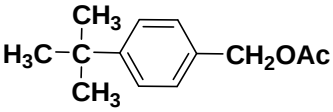
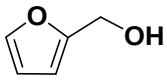
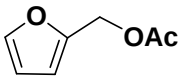
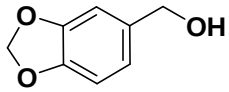
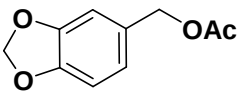
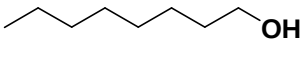
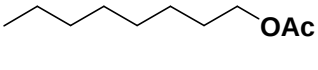
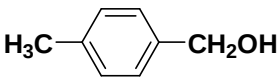
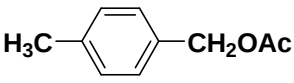
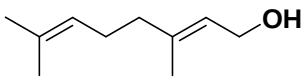
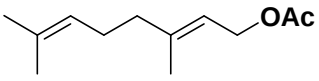
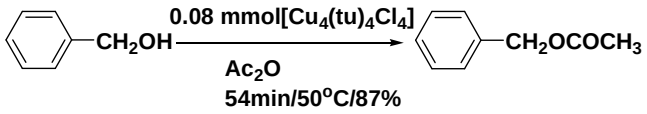
TABLE 1 : Acetilation of alcohols with $[Cu_4(tu)_4Cl_4]$

Entry	Substrate	Product	Time(min)	Yield %
1			54	87
2			50	90
3			49	88
4			78	91
5			65	86
6			80	90
7			63	92
8			65	94
9			70	89
10			76	93
11			80	86
12			52	90

All reactions were carried out of 50° C and with 0.08 mmol of $[Cu_4(tu)_4Cl_4]$

tic anhydrate could be carried out. The optimization experiments resulted that conversion of 1 mmol benzyl alcohol to benzyl acetate was carried out perfectly with 0.08 mmol of $[Cu_4(tu)_4Cl_4]$ in 50°C within 54 min. This result prompted us to investigate the capability of this system for acetylation of various aliphatic and benzylic

alcohols to their corresponding acetates under the optimized conditions. The results of this investigation are summarized in TABLE 1. As shown, all reactions were completed with 0.08 mmol of $[Cu_4(tu)_4Cl_4]$ within 45-80 min to give the corresponding acetates in 86-94 yields (Scheme).



CONCLUSION

In conclusion, we have developed an efficient and excellent yielding method for the acetylation of alcohols with acetic anhydrate under mild reaction conditions. The reactions are clean and no detectable by product was found. The products are obtained good to high yields and the procedure is easy.

ACKNOWLEDGMENTS

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