

Vanadyl(IV) acetate, a new reusable catalyst for acetylation of alcohols

B.M. Choudary^{*}, M. Lakshmi Kantam, V. Neeraja, Tapasree Bandyopadhyay,
P. Narsi Reddy

Indian Institute of Chemical Technology, Hyderabad 500 007, India

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Abstract

Vanadyl(IV) acetate is found to be an efficient catalyst for acetylation of primary, secondary, tertiary and steroidal alcohols in the presence of acetic anhydride in quantitative yields. The catalyst is recovered quantitatively and re-used. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Vanadyl(IV) acetate; Acetylation; Alcohols; Selectivity; Reusability

1. Introduction

Esters have high potential in industry because of their wide use in fragrances, flavours, surfactants, plasticizers and as solvents [1]. Generally they are synthesised by catalytic acetylation of alcohols with 4-(dimethyl amino) pyridine (DMAP) or 4-pyrrolidinopyridine (PPY) in presence of acid anhydrides or acid chlorides [2,3]. Later there were reports on the acylation of alcohols catalysed by tributyl phosphine (Bu_3P) [4,5], cobalt(II) chloride [6,7], trimethylsilyl trifluoromethane sulfonate [8], scandium trifluoromethanesulfonate [9–11], $\text{Sc}(\text{NTf}_2)_3$ [12] and silica gel supported $\text{Ce}(\text{SO}_4)_2$, $\text{Ti}(\text{SO}_4)_2$, $\text{Fe}_2(\text{SO}_4)_3$ and NaHSO_4 [13].

These methods suffer from inherent disadvantages such as high cost of the catalyst, poor regioselectivity in case of allylic alcohols, elimination byproducts in tertiary alcohols, racemization of optically active alcohols, epimerization of steroids and tedious work-up procedures etc. We reported recently [14] that terminal olefins were converted selectively towards the Markonikov's product, 1-methyl alkyl acetate without isomerization using vanadium oxide in presence of trifluoroacetic acid. This prompted us to the development of new Lewis acid catalyst bearing acetate ligands on vanadium for acetylation reactions. We deliberately devised and report herein a heterogeneous system, in which vanadyl(IV) acetate, a powerful Lewis acid catalyst almost practically insoluble in the chosen solvent medium, acetonitrile, for acetylation of alcohols with acetic anhydride with high

^{*} Corresponding author. Tel. +91-40-717-0921; Fax: +91-40-717-3387; E-mail: iict@ap.nic.in

yields and consistently active for several cycles by simple filtration. Incidentally, this forms one of the few reports on heterogenisation of homogeneous system manoeuvred by simple insolubility principle to evolve and act as a truly 'heterogeneous system'.

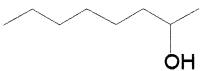
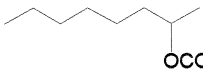
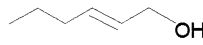
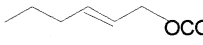
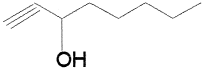
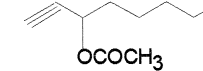


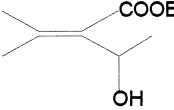
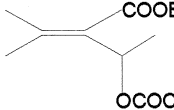



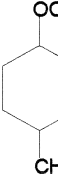
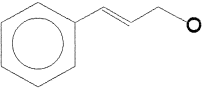
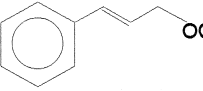
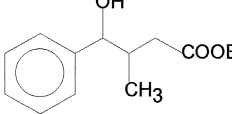
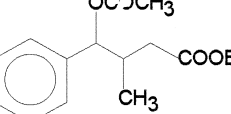
2. Experimental

2.1. Preparation of the catalyst

Vanadyl(IV) acetate was prepared by refluxing vanadium(V) oxide (18.2 g) in excess acetic

Table 1

Direct acetylation of alcohols with acetic anhydride catalysed by vanadyl acetate

ENTRY	SUBSTRATE	PRODUCT	YIELD(%) ^a
1			100
2			75
3			88
4			100
5			100
6			99
7			100
8			100
9			100
10	(-) Menthol	Menthyl acetate	100 ^b , 80 ^c , NR ^d
11	(+)-endo-Norborneol	Norbornyl acetate	100
12	Phenol	Phenyl acetate	85

a) Determined by ¹H NMR, b) [α]_D = -78.8 (Lit; -80.5), ee 98%, c) With

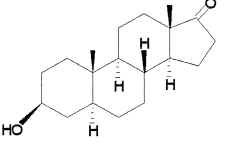
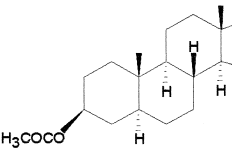
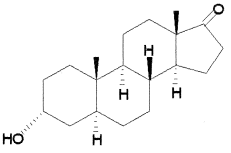
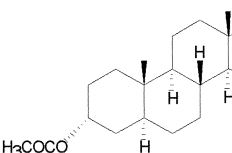
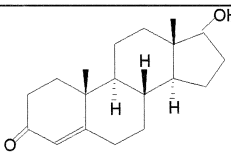
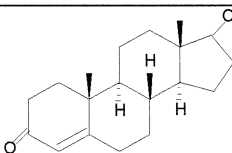
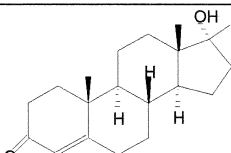
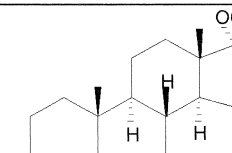
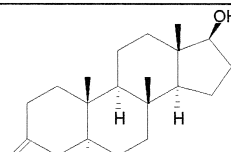
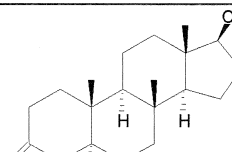
recovered catalyst, d) Without catalyst

anhydride (50 ml) for 1 h. The solid product was then filtered, washed with CHCl_3 and dried under vacuum at room temperature for 1 h (yield 35 g, 95%) [15].

2.2. Acetylation reaction

The alcohol (2 mmol), acetic anhydride (3 mmol) and the catalyst (0.2 mmol) were stirred

Table 2
Vanadyl acetate catalysed acetylation of steroids^a

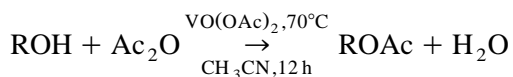
Entry	Substrate	Product	Yield (%) ^b
1			100
2			99.9
3			100
4			100
5			100

a) All reactions were performed using 2mmol of alcohol, 0.2mmol of catalyst in acetonitrile (5ml) at 70°C, 12h, b) Determined by ¹H NMR.

in acetonitrile (5 ml) at 70°C for 12 h. The catalyst was then filtered and kept for another cycle. The filtrate was concentrated and subjected for ^1H NMR spectroscopy.

3. Results and discussion

The conversion of a variety of alcohols, such as primary, secondary, tertiary and steroidal, to the corresponding esters was simply achieved quantitatively by treatment of the alcohol with 1.5 equiv. of acetic anhydride at 70°C for 12 h in the presence of 10 mol% of the catalyst.



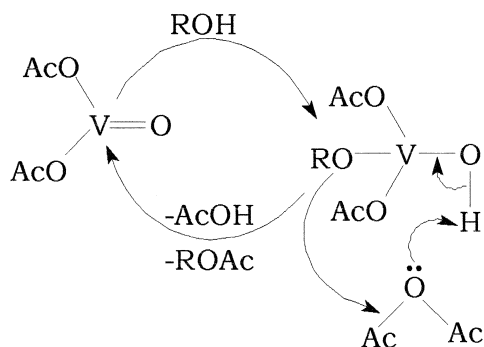
The results which are compiled in Tables 1 and 2 have shown distinct characteristics not chronicled in the earlier reports in the reactivity and selectivity, when encountered with varied alcohols.

The advantages of using this catalyst over the other catalysts can be summarised as follows: vanadium is cheap and easily available. Secondary and tertiary alcohols which show less tendency for acetylation are easily acetylated with the present system. It is significant to notice that tertiary alcohols are acetylated to corresponding acetates selectively without any elimination product, while the acid sensitive substrates such as allylic alcohols without any migration of double bond. Other important features worthy to describe are the acetylation of optically active alcohols without any loss of optical purity as demonstrated in menthol and sterols. Selective acetylation of hydroxy carbonyl compounds is achieved without the formation of α,β -unsaturated carbonyl compounds due to the elimination of the resulting acetate.

The most significant achievement is the reusability of the deliberately chosen heterogeneous salt of transition metal catalyst for several number of cycles with almost constant activity. The famous Lewis acid catalyst, anhydrous aluminium chloride employed in Friedel–Crafts

reaction almost trigger the reaction remaining in the solid phase in the liquid–solid reaction. Therefore, we designed Vanadyl acetate suspended in acetonitrile to coax Lewis acid mediated reaction with additional advantage of reuse and recyclability.

The formation of no unusual product like biacetyl, ketene, olefin or acetoacetate in this case obviously ruled out the possibility of any nonionic pathway such as free radical mechanism as proposed in the case of cobalt(II) chloride by Iqbal and Srivastava [7]. The synergetic effect of Lewis and Bronsted acid sites of insoluble solid salt influences the acetylation reaction for higher activity as solid acids and zeolites. Therefore, the most plausible mechanism may be the ionic one as suggested below:



In conclusion, the primary, secondary, tertiary and steroidal alcohols are acetylated easily with high selectivity and yields using vanadyl (IV) acetate as the catalyst. The work widens the scope of using transition metal salts and complexes as such as heterogeneous catalysts invoking insolubility principle.

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