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Short Communication

Novel α-ketoesters from β-diketones via a vanadium-mediated tandem transformation under an oxygen atmosphere

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ABSTRACT

Novel α-ketoesters were conveniently synthesized from acetylacetone and analogs via a vanadium-mediated one-pot tandem process. These advanced α-ketoesters could be selectively prepared under additive-free, mild conditions, viz., 1 atm O_2 pressure and 50–80 °C. DFT calculations were performed to provide insights into the detailed mechanism of the tandem transformation.

1. Introduction

α-Ketoesters are key intermediates for the synthesis of important substances such as optically active compounds, proteinase inhibitors and heterocycles [1]. Strategies for the one-pot synthesis of α-ketoesters include the addition of Grignard reagents to oxalates or oxalyl chlorides and the Pd-catalyzed double carbonylation of halides [2,3]. However, these methodologies and related approaches often require harsh conditions [4] (e.g., low temperature [2], high CO pressure [3], and use of toxic SeO_2 [5]) and additives [6], which often result in relatively low atom efficiency.

Tandem reactions are powerful tools in green synthesis because of their step economy, operational simplicity and environmental friendliness [7]. Furthermore, one-pot tandem protocols facilitate the preparation of novel compounds that are inaccessible by conventional step-by-step approaches [8]. Thus, many precious metals (e.g., Pd, Ru, Rh, Ir, and Au) [8], small molecules (e.g., H_2O and cinchona alkaloid derivatives) [7,9] and enzymes [10] have been extensively explored in tandem catalysis.

Vanadium, which plays a vital role in chemistry and life sciences, is abundant and relatively inexpensive. Since the discovery of vanadium-dependent haloperoxidase (V-HPO) by Vilter in 1983, vanadium complexes have gained increasing attention for their catalytic potential [11–13]. To date, these complexes have been widely used as catalysts in addition, condensation, cyclization, and oxidation reactions owing to the Lewis acidity and redox capabilities of V^{5+} and V^{4+} [14,15]. The inherently multifunctional nature of vanadium makes it a good candidate for a catalyst in tandem reaction. However, the use of vanadium catalyst in O_2-driven green tandem process remains relatively unexplored probably because of reaction complexity and catalyst compatibility issues [8]. Herein, we report the first example of the facile synthesis of novel advanced α-ketoesters via a vanadium-catalyzed one-pot tandem process using O_2 as the terminal oxidant.

2. Experimental

2.1. General

All chemicals were commercially available and used without further purification. FT-IR spectra of samples were measured on an Avatar-370 spectrometer. UV–Vis spectra of the oxovanadium complexes were recorded with the Shimadzu UV-2450 UV–Vis spectrophotometer. ^1H NMR and ^{13}C NMR spectra of the isolated products were recorded on a Bruker 500-MHz NMR spectrometer. Gas chromatography was run on Agilent 6890 equipped with a DB-5 (30 m × 0.25 mm × 0.25 μm) column. Mass spectra were performed on a Varian Saturn 2100T GC-MS instrument. Density functional theory calculations for the key species at the B3LYP/6-31 + G(d) level have been performed on the Gaussian 03 software package.

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2.2. Synthesis of catalysts

Oxovanadium complexes were prepared by a modified method reported in the literature using 8-hydroxyquinoline (Q) and its halogen-substituted derivatives as the model ligands [16]. A mixture of 30 wt.% aq. H_2O_2 (10 mmol) and 10 mL tetrahydrofuran was added into a three-necked flask containing V_2O_5 (5 mmol) and 10 mL water. Then a solution of 8-hydroxyquinoline (Q, 20 mmol), 5-chloro-8-hydroxy-7-iodoquinoline (Q′, 20 mmol) or 5,7-dichloro-8-hydroxyquinoline (Q″, 20 mmol) in tetrahydrofuran (40 mL) was added and the pH value of the solution was adjusted to 6–7 with ammonia. After refluxing for 2 h, the resulting solution was filtered to give black 8-quinolinolato vanadium complex after washing for three times with ethanol. Bis(8-hydroxyquinolinato) oxovanadium (**Q_2VO**), **Q′$_2$VO** and **Q″$_2$VO** were obtained as black powders in 70%–79% yield.

For comparative studies, we used manganese complexes due to their cheapness, versatility in oxidation, and potential applicability as bifunctional redox-Lewis acid catalysts in tandem process [17]. Bis(8-hydroxyquinolinato) manganese (**Q_2Mn**) was prepared from 5 mmol $Mn(OAc)_2$ and 10 mmol 8-hydroxyquinoline ligand in tetrahydrofuran by the procedure described above. **Q_2Mn** was obtained as a pale yellow powder in 68% yield.

2.3. Transformation of β-diketones

A mixture of acetylacetone (58 mmol) and catalyst (0.07–0.14 mmol, unless otherwise stated) was placed into a three-necked flask. Then the one-pot tandem reaction was performed at 80 °C or specific temperature for the appropriate time under 1 atm O_2 supplied continuously by a commonly used water-seal system [18]. A small amount of mixture was taken out using a syringe. After centrifugation, the mixture was analyzed with an Agilent-6890 gas chromatograph. The identification of products was done by GC-MS (Varian Saturn 2100T; injector temperature: 250 °C, column temperature from 80 °C to 200 °C for $\beta = 7$ °C/min). The resulting product was purified by silica gel column chromatography using a mixed solvent of n-hexane and ethyl acetate (3:1, v/v) as the eluent. The isolated product was determined by ^{13}C NMR (125 MHz, $CDCl_3$), ^1H NMR (500 MHz, $CDCl_3$), GC-MS and FT-IR analysis. Transformation of other β-diketones was performed according to the procedure described above.

3. Results and discussion

3.1. FT-IR spectra of samples

The FT-IR spectra of vanadium complexes **Q_2VO**, **Q′$_2$VO** and **Q″$_2$VO** are shown in Fig. 1. The characteristic stretching frequencies for 8-hydroxyquinoline ligands can be observed at 1566–1574 ($\nu_{(C=N)}$), 1483–1497 cm^{-1} ($\nu_{(C=C)}$), 1450–1466 cm^{-1} ($\nu_{(C=C)}$) and 1369–1377 cm^{-1} ($\nu_{(C-N)}$), respectively [19,20]. It is noteworthy that **Q_2VO**, **Q′$_2$VO** and **Q″$_2$VO** showed strong V=O stretch around 960 cm^{-1} (955, 962 and 960 cm^{-1}, respectively), indicative of mononuclear complexes [21]. Complex **Q_2Mn** also shows major bands between 1300 and 1600 cm^{-1}, which correspond to characteristic stretching frequencies of 8-hydroxyquinoline ligand (Fig. A. 1).

3.2. Tandem transformation of β-diketones under O_2

We began our studies by investigating the influence of different vanadium and manganese catalysts on the tandem reaction of acetylacetone (acacH). The results of these studies are shown in Table 1. When catalyzed by **Q_2VO**, the transformation of acacH proceeded at 80 °C under 1 atm O_2 to give a new α-ketoester, 4-oxo-2-penten-2-ylpyruvate (**3**), in relatively high yield (37.4%, Table 1, entry 1). The structure of **3** was unambiguously identified by ^{13}C NMR, ^1H NMR, GC-MS and FT-IR analysis. Other metal salts studied were shown to be less effective in the tandem process (entries 10–13). In the absence of catalyst or O_2, the tandem

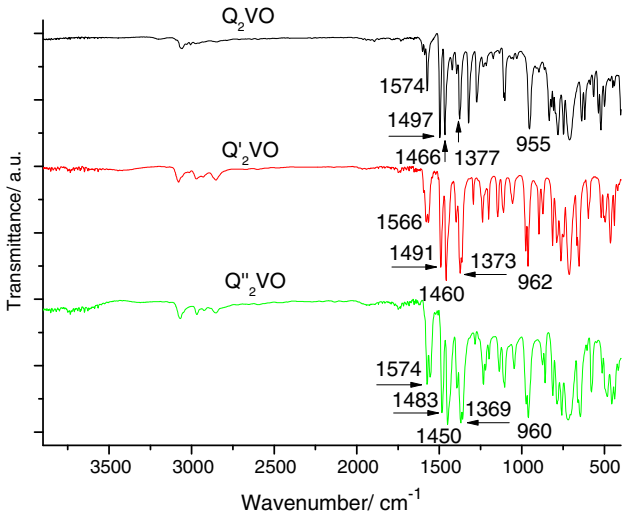

Fig. 1. FT-IR spectra of **Q_2VO**, **Q′$_2$VO** and **Q″$_2$VO**.

reaction hardly proceeded, whereas the presence of pyridine exhibited only minor influence on the yield of **3** (entries 3, 14 and 15). It is interesting to note that the reaction leading to **3** catalyzed by **Q_2VO** can proceeded at lower temperatures (50–60 °C, entries 5 and 6), although the conversion of acacH was slow. These results show that the vanadium complex can efficiently serve as a multifunctional catalyst for the tandem transformation of acacH to give **3** and has promising potential as a biomimetic activator of O_2 at mild temperatures.

Comparison of entry 4 with entry 7 in Table 1 showed that Q greatly improved the catalytic efficiency of vanadium compounds (per V atom). In addition, a manganese center could also be tuned by Q to improve the selectivity for product **3** (entries 10 and 11), which is consistent with our recent report on the green oxidation of alcohols using a Q derivative catalyst Q_3Mn [16]. Not surprisingly, halogen-substituted ligands Q′ and Q″ inhibited the activity of the catalyst in the tandem reaction (entries 2, 8 and 9), probably because of the electron-withdrawing effect of the halogen substituents.

Next, we explored the scope of the tandem transformation with a variety of β-diketones using **Q_2VO** as the catalyst (Table 2). Interestingly, the tandem reaction seemed to be substrate-selective. Fairly good yields were obtained when using analogs bearing an acacH subunit (entries 1–3), while ethyl acetoacetate, which has no acacH subunit, was unreactive (entry 7). Other β-diketones containing α-CF_3 or phenyl

Table 1
Tandem transformation of acacH mediated by various catalysts under 1 atm of O_2[a].

Entry	Catalyst (mmol)	Time (h)	T (°C)	Conversion (%)[b]	Selectivity (%)[b]
1	Q_2VO (0.14)	8	80	47.8	78.2
2	Q_2VO (0.07)	8	80	20.7	76.8
3[c]	Q_2VO (0.07)	8	80	14.7	76.2
4	Q_2VO (0.07)	8	70	16.9	76.3
5	Q_2VO (0.07)	8	60	3.3	72.7
6	Q_2VO (0.07)	8	50	0.4	72.5
7	V_2O_5 (0.07)	8	70	13.5	68.0
8	Q'_2VO (0.07)	8	80	18.6	53.6
9	Q''_2VO (0.07)	8	80	15.7	49.5
10	Q_2Mn (0.1)	8	80	2.1	66.7
11	$Mn(OAc)_2$ (0.1)	8	80	4.4	34.1
12	$Cu(OAc)_2$ (0.1)	24	80	0.8	<15.0
13	$FeCl_3$ (0.1)	24	80	0.6	0
14	None (0)	24	80	Trace	0
15[d]	Q_2VO (0.07)	8	80	0	0

[a] AcacH (58 mmol), catalyst (0.07–0.14 mmol), O_2 (1 atm), 8–24 h, 50–80 °C.
[b] Determined by GC.
[c] Pyridine (6 mmol) was added.
[d] The reaction was performed under 1 atm of N_2.