Aerobic oxidation of α-hydroxycarbonyls catalysed by trichlorooxyvanadium: efficient synthesis of α-dicarbonyl compounds

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α-Hydroxycarbonyls were efficiently oxidized into α-dicarbonyls using a catalytic amount of trichlorooxyvanadium under an oxygen atmosphere.

α-Dicarbonyl compounds are important materials in synthetic organic chemistry.[1] They have been used as substrates for benzylic acid rearrangement[2] and starting materials for syntheses of heterocyclic compounds.[3] α-Dicarbonyl compounds are frequently obtained by the oxidation of α-hydroxycarbonyl precursors. Due to the sensitivity of the α-dicarbonyl compounds, special reagents and reaction conditions are required to prevent side reactions during the oxidation of the α-hydroxycarbonyls.[1] Although a number of methods have been developed to achieve this transformation, most of them suffer from drawbacks such as the use of stoichiometric amounts of corrosive acids or toxic metallic compounds that generate undesirable waste materials.†

We now describe the chemoselective aerobic oxidation of α-hydroxycarbonyls to α-dicarbonyls catalysed by high valent vanadium.‡

During the course of our study of the oxyvanadium-catalysed cleavage of α-hydroxy ketones, we found that the reaction of 2-hydroxycyclooctanone with a catalytic amount of dichloroethoxyoxyvanadium [VO(OEt)Cl₂] in MeCN under an oxygen atmosphere efficiently afforded cyclooctane-1,2-dione.[4]

We further examined the reaction, and found that α-dicarbonyl compounds could be efficiently obtained when trichlorooxyvanadium (VOCl₃) was used as the catalyst (Scheme 1).

First, we chose benzoin as the substrate and examined the reaction with several high valent vanadium catalysts in MeCN under an oxygen atmosphere (Table 1). Benzil was obtained in all cases, and the best result was obtained when VOCl₃ was used as the catalyst (run 2).

We then examined the reaction of benzoin with a catalytic amount of trichlorooxyvanadium in several solvents (Table 2). As noted in runs 1 and 2, MeCN and acetone are good solvents for this reaction.

The reaction of several α-hydroxy ketones with a catalytic amount of VOCl₃ in MeCN under an oxygen atmosphere provided the α-diketones in excellent yields.§ In all cases, the α-diketone was the sole product and no by-products were observed. These results are summarized in Table 3. The reaction
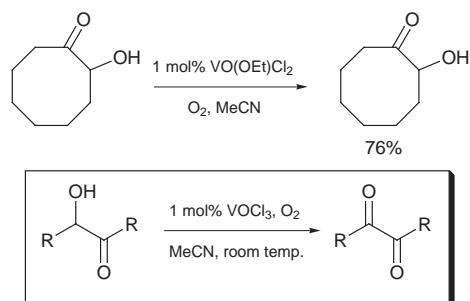
Table 1 Reaction with different catalysts

Run	Catalyst	t/h	Yield (%)
1	VO(OEt)Cl₂	1.5	94
2	VOCl₃	1.5	95
3	VO(OEt)₃	103	76
4	VO(acac)₂	127.5	76

Table 2 Reaction with different solvents

Run	Solvent	t/h	Yield (%)
1	MeCN	1.5	95
2	Acetone	2.5	94
3	CH₂Cl₂	21.5	84
4	AcOH	4.5	68
5	MeCN–H₂O (4:1)	307	57
6	Benzene	210.5	55

Table 3 Reaction with different α-hydroxy ketones

Entry	α-Hydroxy ketone	t/h	Yield (%)
1	R = Ph	1.5	95
2[a]	R = Ph	11	89
3	R = 4-ClC₆H₄	1.5	quant.
4	R = 4-MeOC₆H₄	1.5	quant.
5	R = C₉H₁₉	12	quant.
6	R = CH₂=CH(CH₂)₇	5.5	quant.
7[b]	R = C₁₅H₃₁	13.5	quant.
8	R = cyclohexyl	20	95
9	R–R = (CH₂)₁₀	8.5	quant.
10	R–R = (CH₂)₁₃	22.5	95
11		114	quant.

[a] The reaction was carried out in air. *[b]* The reaction was carried out under reflux.

Scheme 1

R = hexyl 95%
R = Ph 85%
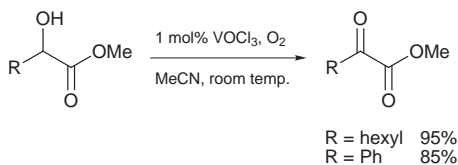
Scheme 2

of benzoin with a catalytic amount of VOCl₃ in MeCN in air also gave benzil in good yield (entry 2). It took longer to complete the reaction in the cases of the α-diketones having aliphatic substituents (entries 5–11). Interestingly, alcohols without a carbonyl moiety at their α-position did not react under the same conditions. α-Hydroxy esters were also efficiently oxidized to α-keto esters (Scheme 2).

As mentioned in a previous paper,[4] this reaction is not a simple radical oxidation, because this reaction was not influenced by a radical inhibitor.¶ A stoichiometric amount of VOCl₃ reacted with benzoin to afford benzil in the absence of oxygen (Scheme 3). This result means that molecular oxygen acts as a co-oxidant and reoxidizes the low valent vanadium that is formed.

We observed that the color of the reaction mixture was dark yellow at first, and then turned green in most cases. The 'green' of the reaction mixture strongly suggests the presence of V^IV
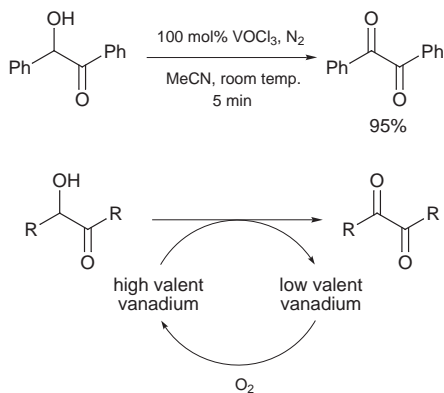
Scheme 3

species. Further study concerning aspects of the mechanism is currently underway.

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Notes and references

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