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LETTERS

Dirhodium(II) carboxylate-catalysed oxidation of allylic and benzylic alcohols

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Abstract—Allylic and benzylic alcohols are oxidised to the corresponding carbonyl compounds using *tert*-butyl hydroperoxide, preferably in stoichiometric amounts, and dirhodium(II) tetraacetate as catalyst (1 mol%) in dichloromethane at ambient temperature. © 2001 Elsevier Science Ltd. All rights reserved.

The oxidation of alcohols to the corresponding carbonyl compound is a transformation that is fundamental to synthetic organic chemistry, and numerous reagents, many of them metal based, have been developed to carry out this important reaction.[1] However, with the increasing emphasis on protocols that are acceptable from the economic and ecological point of view, recent efforts have focused on systems which employ metals only in catalytic amounts together with an inexpensive stoichiometric oxidant such as a peroxide, molecular oxygen or, ideally, air. Recent examples include systems based on ruthenium [Ru(II),[2,3] Ru(III),[4,5] or perruthenate[6–8]], copper,[9–11] and palladium(II) acetate.[12–14] Much less common is the use of rhodium based catalysts,[15] despite the fact that they have long been known to catalyse such processes as allylic oxidation.[16–18] In view of our interest in dirhodium(II)-catalysed processes in organic synthesis, we initiated a study into the use of dirhodium(II) carboxylates as catalysts for oxidation reactions.[19] We now report that allylic and benzylic alcohols are readily oxidised to the corresponding carbonyl compounds using *tert*-butyl hydroperoxide (TBHP) in the presence of catalytic amounts of dirhodium(II) tetracarboxylates.

When a dichloromethane solution of 2-cyclohexenol was stirred with *tert*-butyl hydroperoxide (ca. 1 mol%) and $Rh_2(OAc)_4$ (1 mol%) either open to the air or under an oxygen atmosphere, slow oxidation to 2-cyclohexenone occurred. No significant oxidation occurs in the absence of the rhodium complex. Although the reaction, which was monitored by GC, was faster under O_2 than air, it was only ca. 40% complete even after 120 h,[20] by which time it appeared that the catalyst was no longer active (colour change to yellow). Changing to a catalyst with more strongly electron-withdrawing carboxylate ligands, such as $Rh_2(OCOCF_3)_4$ or $Rh_2(OCOC_3F_7)_4$, resulted in a longer lived catalytic species (>3 weeks). However, the rate of oxidation of 2-cyclohexenol was slower than with $Rh_2(OAc)_4$ itself, and using $Rh_2(OCOCF_3)_4$ as catalyst, 2-cyclohexenone was formed in ca. 55% yield only after 20 days. Therefore, in order to decrease the inconveniently long reaction times, the amount of oxidant was increased; with 100 mol% oxidant and 1 mol% $Rh_2(OAc)_4$, the oxidation was >85% complete after 24 h.

Having established useful reaction conditions, the method was applied to other alcohols. The results, which are shown in Table 1, show that the method is generally applicable to a range of secondary allylic and benzylic alcohols, and gives the corresponding ketones in good yield. Most of the oxidations are complete within 24–30 h, although 1-phenylethanol and 1-phenyl-butanol are oxidised more slowly.

Primary allylic and benzylic alcohols are also oxidised under the reaction conditions, although the yields of the corresponding aldehydes (25–45% by GC) are considerably lower, due to by-product formation. Unactivated primary and secondary alcohols such as 2-hexanol or cyclohexanol were not efficiently oxidised under the above conditions.

In summary dirhodium(II) tetraacetate is an efficient catalyst for the oxidation of secondary allylic and ben-

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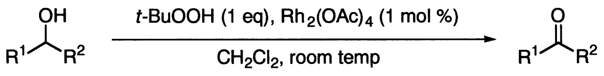
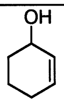
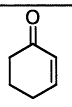
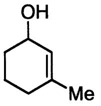
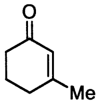
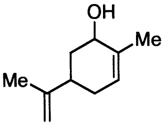
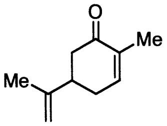
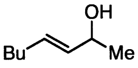
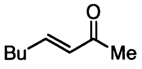
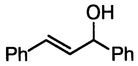
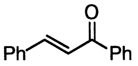
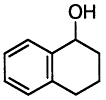
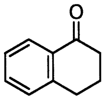
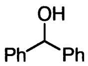
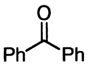
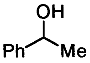
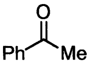
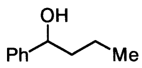
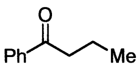
Table 1. Oxidation of secondary allylic and benzylic alcohols catalysed by $Rh_2(OAc)_4$ using TBHP[a]



Substrate	Time (h)	Product(s)	GC Yield (%)[b]	Isolated Yield (%)
	31		75	41
	31		90	65
	30		49	37
	48		70	52
	28		92	88
	48		69	63
	24		-	97[c]
	48		-	48[c,d]
	48		-	39[c,e]

[a] *Reaction conditions:* **CAUTION**: all mixtures involving peroxides should be handled using appropriate precautions. A solution of alcohol (ca. 1.0 g), and TBHP (100 mol%, 5–6 M in decane) in dichloromethane (0.1 M) was added to a sealed vessel containing $Rh_2(OAc)_4$ (1 mol%), which had been twice evacuated and flushed with O_2. The reaction mixture was stirred under an O_2 atmosphere at room temperature for the time indicated.

[b] Yields were determined by GC analysis using an internal standard technique.

[c] Thin layer chromatography was employed to follow reaction progression; only preparative scale reactions were performed.

[d] 45% of the starting 1-phenylethanol was recovered from column chromatography.

[e] 55% of the starting 1-phenylbutanol was recovered from column chromatography.

zylic alcohols using *tert*-butyl hydroperoxide as oxidant.

Acknowledgements

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