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Aldehydes from Pd-catalysed oxidation of terminal olefins

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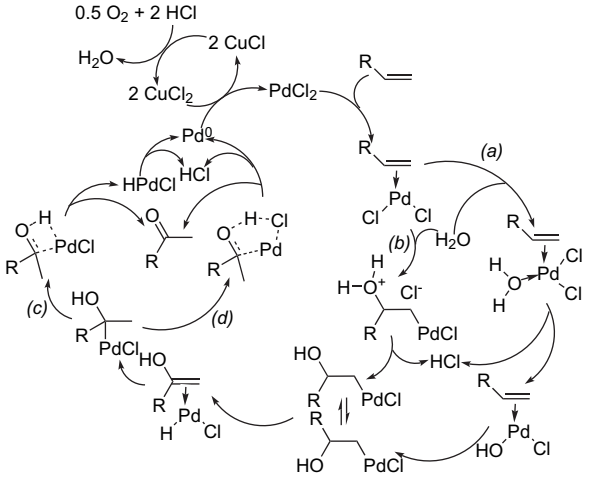
1. Introduction

The Pd^{II}-catalysed oxidation of alkenes to carbonyl compounds, usually referred to as the Wacker reaction,[1,2] is one of the most well-known reactions mediated by palladium, and has extensive synthetic applications.[3–6] This process involves coordination of the alkene to Pd^{II} and, subsequently, reaction of the η^2-Pd–alkene complex with water to afford, in the majority of cases, methyl ketones from terminal alkenes.[3–5,7] Scheme 1 depicts the simplified mechanism with $PdCl_2$ as the catalyst, and when catalytic amounts of copper chloride are used with oxygen to regenerate the active Pd^{II} species. In this scheme, the hydroxypalladation follows Markovnikov's rule; its stereochemistry, *syn* (path a) or *anti* (path b), depends on the experimental conditions,[3,8–11]



Scheme 1.

Keywords: Palladium; Alkenes; Aldehydes; Wacker reaction; Oxidation; Anti-Markovnikov addition.
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and remains a matter of debate.[12] Recently, other steps have also been the subject of investigations,[13,14] especially the formation of the ketone from ClPdCR(OH)Me (Scheme 1) with the proposal of a halide-mediated reductive elimination (path d), rather than the usually accepted β-hydride elimination (path c).[14]

The Wacker reaction has been so widely used in organic synthesis that terminal alkenes may be viewed as masked ketones. Nevertheless, aldehydes are sometimes produced but, except from particular substrates, usually in low yields.[8,15–17] Seeing the importance of aldehydes in synthesis, it seems of interest to highlight, with an overview, the investigations that have been carried out to obtain anti-Markovnikov regioselectivity in the Pd-catalysed oxidations of terminal alkenes. This is the aim of the present review. Most of the reports describe the oxidation via a Wacker-type procedure, but a few studies disclose methods that do not involve the hydroxypalladation as the key step, hence the organisation of the review with, mainly, also a chronological account of the reports.

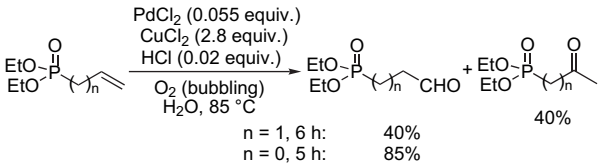
2. Wacker-type reactions

This section will not be limited to catalytic methods using water as the nucleophile and the association of copper salt/oxygen to regenerate the Pd^{II} active species, but will include all Pd procedures for which a hydroxy-, alkoxy- or acetoxypalladation is suspected as an intermediate step leading to the aldehyde.

2.1. Hydroxypalladations

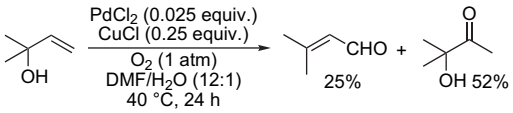
A few papers report the formation of the aldehyde with fair-to-high selectivity from the hydroxypalladation of simple terminal alkenes, but using stoichiometric quantities of a palladium salt[18] or with very low conversion of the substrate.[19] Catalytic procedures leading to aldehydes with useful yields have been disclosed only from substrates having a second chelating fragment, i.e., a heteroatom or unsaturation.

2.1.1. 1-Alkenes with P atom in α- or β-position. To our knowledge, the first efficient synthesis of aldehydes from the Pd-catalysed oxidation of terminal alkenes is due to Sturtz and Pondaven-Raphalen, who used vinylic and allylic phosphonates as the substrates (Eq. 1).[20] The authors ascribed the remarkable regioselectivity obtained from the vinylic substrate to the electron-withdrawing properties of the diethylphosphonate group. We suspect that the formation of aldehydes is also favoured by coordination of the phosphonate moieties to the palladium atom.



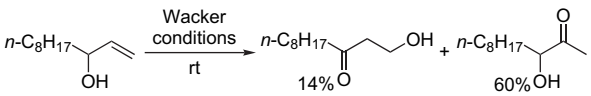
(1)

2.1.2. 1-Alkenes with O atom in β-position. In 1984, Tsuji disclosed briefly in a review that the oxidation under Wacker conditions of a tertiary allylic alcohol, namely 1-vinylcyclohexanol, led to low amounts of 1-acetylcyclohexanol and 2-cyclohexylideneacetaldehyde.[4] A similar observation has subsequently been reported by Brégeault et al. from 2-methylbut-3-en-2-ol (Eq. 2),[21] and they explained the formation of the aldehyde by isomerisation of the substrate[22] to the corresponding primary allylic alcohol followed by oxidation of the hydroxy group.[23]

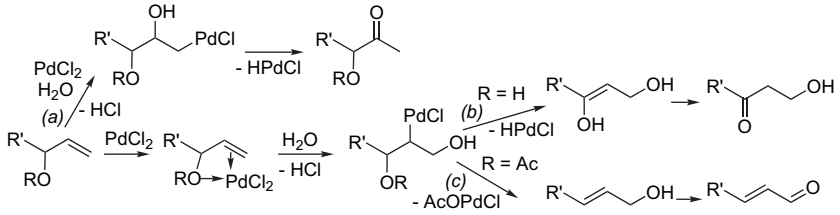


(2)

Tsuji reported, also without comment, that, at room temperature under Wacker conditions, 1-undecen-3-ol led to a mixture of 1-hydroxyundecan-3-one and 3-hydroxyundecan-2-one (Eq. 3), while 2-undecenal and 3-acetoxyundecan-2-one were isolated from 3-acetoxy-1-undecene (Eq. 4).[4] These methyl ketones are formed via the usual Wacker-type mechanism (Scheme 2, path a and Scheme 1). We suggest that the β-hydroxyketone (Eq. 3) ensues from the addition of water to the complex formed by coordination of the hydroxy group to palladium followed by the intramolecular abstraction by palladium of the hydrogen in C-3 to intermediately afford the hydroxyenol, as depicted in Scheme 2, path b. Such a reaction pathway has been proposed for the formation of β-hydroxypropanal from allyl alcohol and a stoichiometric amount of Li_2PdCl_4 in aqueous solution.[24] As for the α,β-unsaturated aldehyde (Eq. 4), the hydroxypalladation of the allylic acetate would be followed by the β-OAc elimination[25] and oxidation of the resulting allylic alcohol[23] (Scheme 2, path c).[26] Another possibility would be the formation of an η^3-allylpalladium intermediate followed by nucleophilic addition of water to afford the allylic alcohol.



(3)



Scheme 2.

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