Catalytic Oxidation of Alk-1-enes to Aldehydes

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Aldehydes are the major products of the catalytic oxidation of alk-1-enes with air using a catalyst that comprises $(MeCN)_2PdClNO_2$, $CuCl_2$, and a tertiary alcohol.

Selective catalytic oxidations of alkenes with molecular oxygen are commercially important processes.[1] Indirect methods *via* alkyl hydroperoxides are widely used but have the drawback of stoicheiometric coproduct formation.[2] Recently, new catalysts for the oxidation of alkenes to ketones based on the nitro–nitroso redox couple lacking the co-oxidation problem have been described.[3]

We now report the first successful application of a modified palladium(II)-nitro complex as a catalyst for the oxidation of alk-1-enes to aldehydes. The oxidation catalyst $[(L)Pd\text{–}NO_2]$ (**1**)‡ was obtained as a brown solid by heating a mixture of $(MeCN)_2PdClNO_2$[3] and $CuCl_2$ (molar ratio 1:4) in t-butyl alcohol at 55 °C. Unexpectedly, we found that oxygen-saturated solutions of (**1**) in t-butyl alcohol oxidize dec-1-ene at 30 °C to a mixture of decan-1-al and decan-2-one (ratio 60:40) in 280% yield (based on Pd) in 66 min (Table 1, entry 1). The results of this oxidation reaction with several alkenes under various conditions are summarized in Table 1.

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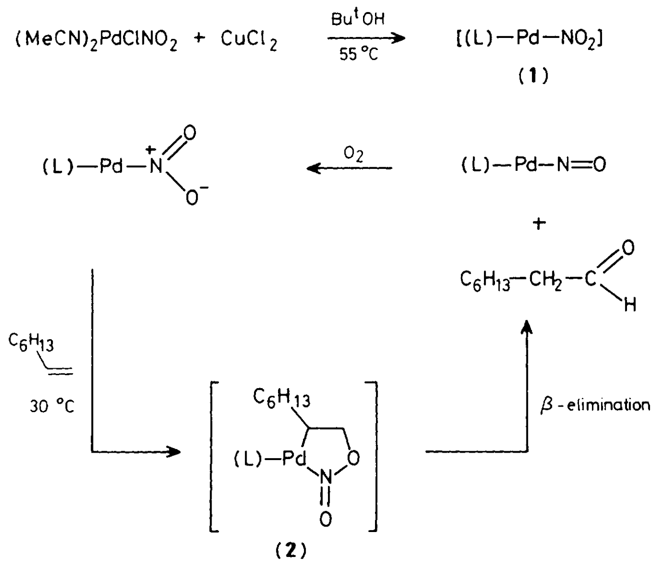
‡ The exact constitution of the catalyst complex is at present uncertain. In structure (**1**) the symbol L indicates all ligands (MeCN, $CuCl_2$, Me_3COH) essential for the formation of the active catalyst.

Table 1. Oxidation of alk-1-enes.

Entry	Alkene (mmol)		Pd/Cu[a] mmol/mmol	Solvent	Reaction time (h)	Yield (mmol)	Product molar ratio[b]
1	Dec-1-ene	(0.41)	0.04/0.16	Bu^{t}OH	1.10	0.11	60/40
2	Dec-1-ene	(0.41)	0.04/0.04	Bu^{t}OH	2.06	0.28	18/82
3	Dec-1-ene	(0.71)	0.05/0	Bu^{t}OH	0.15	0.02	0/100
4	Dec-1-ene	(0.42)	0.04/0.18[c]	Bu^{t}OH	3.00	0.04	70/30
5	Dec-1-ene	(0.40)	0.04/0.18	Me_2CHOH	20.00	0.30	0/100
6	Dec-1-ene	(0.38)	0.04/0.18	$EtCMe_2OH$	1.12	0.08	38/62
7	Dec-1-ene	(0.40)	0.04/0.18[d]	Bu^{t}OH	2.00	0.11	70/30
8	Styrene	(0.85)	0.05/0.20	Bu^{t}OH	2.00	0.08	100/0
9	Oct-1-ene	(0.44)	0.04/0.17	Bu^{t}OH	2.52	0.19	55/45
10	4-Methyl-pent-1-ene	(0.77)	0.05/0.18	Bu^{t}OH	1.35	0.10	60/40
11	3-Methyl-non-1-ene	(0.38)	0.05/0.20	Bu^{t}OH	3.20	0.07	18/82
12	Dec-1-ene		0.05/0.20[e]	Bu^{t}OH	3.63	0.23	50/50
13	Allyl alcohol	(0.55)	0.04/0.20	Bu^{t}OH	0.30	0.40	[f]

[a] $(MeCN)_2PdClNO_2$–$CuCl_2$. [b] Aldehyde/methyl ketone. [c] 0.19 mmol KNO_2 added. [d] $(Me_2CHCN)_2PdClNO_2$ instead of $(MeCN)_2PdClNO_2$ used for catalyst preparation. [e] 0.21 mmol $AgBF_4$ added after 1.35 h. [f] The product comprises 3-t-butoxypropanal and 3-t-butoxypropen-2-ol in a molar ratio of 70/30.



L = $MeCN$–$CuCl_2$–Me_3COH‡

Scheme 1

With linear alk-1-enes an excess of aldehyde is formed when (**1**) is used as the catalyst in t-butyl alcohol as the solvent. Styrene yields phenylacetaldehyde exclusively. The selectivity towards aldehyde depends on the structures of the tertiary alcohol (entry 6) and the nitrile (entry 7) and is sensitive to branching at the allylic position of the alkene. Addition of $AgBF_4$ leads to an increase in oxidation rate but lowers the selectivity. No aldehyde is formed when either tertiary alcohol or $CuCl_2$ is omitted in the catalyst preparation (entries 3 and 5). When $(MeCN)_2PdCl_2$ is used instead of $(MeCN)_2PdClNO_2$ no oxidation reaction is observed and $(MeCN)_2PdClNO_2$–$CuCl_2$ in propan-2-ol leads exclusively to ketones. Small amounts of H_2O ($\leqslant$3 equiv.) have no influence on the selectivity. The alkene isomerization activity of (**1**) is low as only traces of isomeric decenes are formed from dec-1-ene after prolonged reaction times.

On the basis of these results we propose that the aldehyde formation involves an oxygen transfer reaction *via* initial cycloaddition of nitro-palladium complex (**1**) leading to (**2**), followed by β-hydrogen elimination (Scheme 1). Structurally similar cycloadducts have been characterized in the oxidation reaction of alkenes to ketones using $(MeCN)_2PdClNO_2$.[3] As the formal oxidation state of palladium does not change during this oxidation, the role of Cu^{II} salts is essentially different from that in the Wacker oxidation.[4] A hetero-bimetallic catalyst complex comprising Cu^{II} salt and tertiary alcohol might be present, which determines the stereoselectivity in the cycloaddition step.

The selectivity for terminal oxidation of alk-1-enes using this new catalyst is in strong contrast with the usual selectivity in metal-catalysed oxidations.[1,2,4] These findings look promising for alk-1-ene functionalization and might lead to an alternative for hydroformylation.[1]

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