

## Oxidation of Olefins to Aldehydes Using a Palladium–Copper Catalyst

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Wacker-like catalysts using *tert*-butyl alcohol as the solvent oxidize terminal olefins to give unusually high selectivities for aldehydes and also provide some insight into the role of copper and oxygen in Wacker-like reactions.

The oxidation of terminal olefins with palladium salts usually affords methyl ketones.<sup>1–3</sup> However, in 1986 it was reported that aldehydes could be obtained using a catalyst comprising (MeCN)<sub>2</sub>Pd(NO<sub>2</sub>)Cl and CuCl<sub>2</sub> in Bu<sup>t</sup>OH, which was proposed to be bimetallic with the NO<sub>2</sub> group intact.<sup>4</sup> Our studies suggest that this catalyst is best described as a Wacker-like oxidation catalyst modified by an alkyl nitrite, and we report an improved version of this catalyst. Moreover, the application of our system to the oxidation of terminal olefins with allylic substituents has led to some insight as to the potential role of the copper co-catalyst in non-aqueous Wacker-like reactions.

At the time of this report, we were independently working with the same Pd/Cu catalyst but in tetrahydrofuran. We added CuCl<sub>2</sub> to (MeCN)<sub>2</sub>Pd(NO<sub>2</sub>)Cl,<sup>5</sup> and cationic analogues<sup>6</sup> in order to slow isomerization of the olefinic double bond,<sup>7</sup> but we found that the oxidation rate acquired a positive dependence on [CuCl<sub>2</sub>]. IR analysis of a mixture of (MeCN)<sub>2</sub>Pd(NO<sub>2</sub>)Cl and CuCl<sub>2</sub> in tetrahydrofuran (THF) revealed that the NO<sub>2</sub> group is immediately transferred first to the copper and then to the olefin to form 2-chloro-1-nitroalkane.<sup>†</sup> Therefore, no metal nitro catalyst is involved in THF solvent.

After this report, we investigated the same reaction in Bu<sup>t</sup>OH and found a much simpler process: when CuCl<sub>2</sub> was added, the nitro group was immediately transferred from

palladium to Bu<sup>t</sup>OH to give *tert*-butyl nitrite. Based on these and other observations, we created a catalyst comprising (RCN)<sub>2</sub>PdCl<sub>2</sub>, CuCl and a chloride salt in a *tert*-alcohol solvent that efficiently oxidizes terminal olefins to give unusually high selectivities to aldehydes (Scheme 1, Table 1). Catalyst lifetimes are very good with no evidence of deactivation. Optional additives include CuCl<sub>2</sub> or *tert*-butyl nitrite, which decrease olefin isomerization although each have undesirable effects as well.<sup>‡</sup> With allyl acetate as the substrate, the identity of the nitrile in the Pd complex influences the total yield whereas the identity of the chloride salt influences the amount of allylic exchange (Table 1).

Selectivities for the oxidation of simple  $\alpha$ -olefins are significantly higher than in standard Wacker-like reactions where typically no aldehyde is produced (Table 1). Replacing CuCl with CuCl<sub>2</sub> leads to a significant induction period for ketone formation, and thus anomalously high aldehyde selectivities are seen at the beginning of the reaction. However, the rate of ketone formation eventually exceeds the rate of aldehyde formation and selectivities are lower at longer reaction times. Better aldehyde selectivities are obtained with various allyl derivatives,<sup>2,3</sup> although exchange of the allylic group with the solvent can occur under certain conditions (see below).

The superficial mechanism of this reaction appears to be very much like that proposed for the Wacker reaction. The Bu<sup>t</sup>OH plays a key role in the selectivity because it apparently behaves as a hindered nucleophile that attacks the palladium-

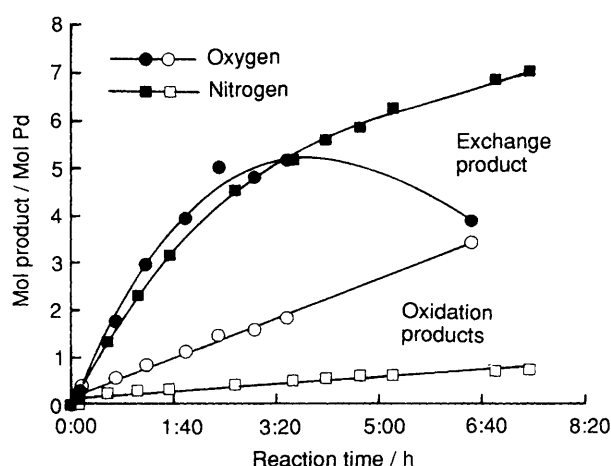
<sup>†</sup> Transfer of the nitro group from Pd to Cu forms (MeCN)<sub>2</sub>PdCl<sub>2</sub> and a mixture of what appear to be two copper nitrate species and a copper nitrosyl species. IR data ([<sup>2</sup>H<sub>8</sub>]THF): Nitrate bands: 1549, 1500, 1300, 1288, 1255 cm<sup>-1</sup>. Nitrosyl band: 1860 cm<sup>-1</sup>. The same mixture is obtained by mixing CuCl<sub>2</sub> and AgNO<sub>3</sub>. The nitrosyl compound could be independently generated by treating CuCl<sub>2</sub> with NOCl in THF. This nitrosyl complex is rapidly converted to the mixture of nitrate species on exposure to oxygen.

<sup>‡</sup> Olefin isomerization is a significant inefficiency with simple  $\alpha$ -olefins, particularly at longer reaction times. Both CuCl<sub>2</sub> and *tert*-butyl nitrite can decrease this, but CuCl<sub>2</sub> tends to give chlorinated byproducts whereas *tert*-butyl nitrite tends to lower the aldehyde selectivity. With allylic ethers and acetates, little if any isomerization is observed so neither CuCl<sub>2</sub> nor *tert*-butyl nitrite are required.

**Table 1** Yields and selectivities for the oxidation of various terminal olefins to aldehydes and ketones

| Substrate                  | Comments                                   | t/h | Conversion (%) | Allylic exchange (%) | Aldehyde select. (%) <sup>d</sup> | Yield ald + ket (%) |
|----------------------------|--|-----|----------------|----------------------|-----------------------------------|---------------------|
| Oct-1-ene <sup>a</sup>     |  | 0.5 | 12             | —                    | 30                                | 8                   |
| Oct-1-ene <sup>a</sup>     |  | 3   | 49             | —                    | 31                                | 38                  |
| Oct-1-ene <sup>a</sup>     | No CuCl                                    | 0.5 | 4              | —                    | 57                                | 1                   |
| Oct-1-ene <sup>a</sup>     | No CuCl                                    | 3   | 56             | —                    | 28                                | 39                  |
| Allyl acetate <sup>b</sup> | Acetonitrile                               | 1   | 100            | 3                    | 75                                | 60                  |
| Allyl acetate <sup>b</sup> | Acetonitrile <sup>c</sup>                  | 1   | 90             | 5                    | 86                                | 56                  |
| Allyl acetate <sup>b</sup> | <i>p</i> -Nitrobenzonitrile                | 1   | 100            | 0                    | 73                                | 75                  |
| Allyl acetate <sup>b</sup> | Benzonitrile                               | 1   | 100            | 0                    | 69                                | 63                  |
| Allyl acetate <sup>b</sup> | <i>p</i> -Methoxybenzonitrile              | 5   | 96             | 0                    | 56                                | 21                  |
| Allyl acetate <sup>b</sup> | MgCl <sub>2</sub> (0.25 mmol) <sup>e</sup> | 1   | 93             | 28                   | 75                                | 58                  |
| Allyl acetate <sup>b</sup> | THF solvent <sup>f</sup>                   | 5   | 42             | 0                    | 27                                | 21                  |
| Allyl acetate <sup>b</sup> | 10% H <sub>2</sub> O–DMF <sup>g</sup>      | 5   | 100            | 0                    | 2                                 | 40                  |

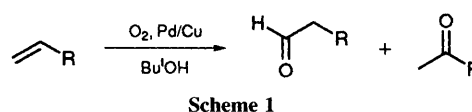
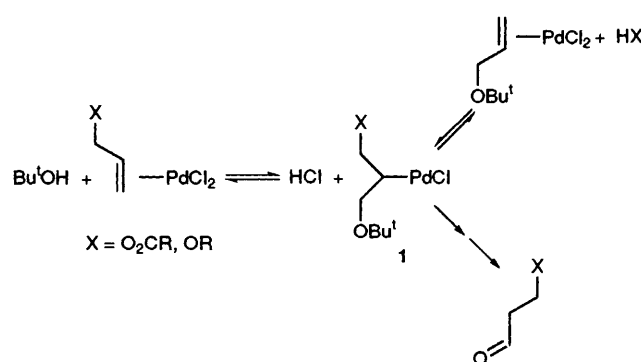
<sup>a</sup> 0.25 mmol (MeCN)<sub>2</sub>PdCl<sub>2</sub>, 1.0 mmol CuCl<sub>2</sub>, 0.5 mmol CuCl, 0.5 mmol LiCl, 7 mmol oct-1-ene, 5 ml Bu<sup>t</sup>OH, 60°C, 40 psi oxygen. Olefin isomerization tends to dominate at >50% conversion. <sup>b</sup> 0.25 mmol PdCl<sub>2</sub>, 1.0 mmol nitrile, 0.5 mmol CuCl, 0.5 mmol NaCl, 10 mmol allyl acetate, 5 ml Bu<sup>t</sup>OH, 60°C, 40 psi oxygen. <sup>c</sup> Same as (b), but 50°C. <sup>d</sup> Mol aldehyde/(mol aldehyde + mol ketone). <sup>e</sup> In place of NaCl. <sup>f</sup> Tetrahydrofuran with MeCN. <sup>g</sup> 0.5 mmol PdCl<sub>2</sub>, 0.5 mmol CuCl, 5.3 mmol allyl acetate, 2.3 ml 10% H<sub>2</sub>O–dimethylformamide, 20°C, 40 psi O<sub>2</sub>. (1 psi ≈ 6.894 kPa).



**Fig. 1** Effect of oxygen on the conversion of allyl ethyl ether to oxidation products (aldehyde + ketone) and exchange product (allyl *tert*-butyl ether) in Bu<sup>t</sup>OH (30°C, 0.05 mol dm<sup>-3</sup> PdCl<sub>2</sub>, 1:4:2:2:4:40 PdCl<sub>2</sub>:MeCN:CuCl:NaCl:CuCl<sub>2</sub>:allyl ethyl ether). Downward curve for exchange product with 80 psi oxygen is due to oxidation of this product.

coordinated olefin at the less-hindered terminal carbon to give an intermediate *sec*-alkyl palladium species **1** which either loses HX to give the exchange product or goes on to give aldehyde (Scheme 2). Competing attack at the more-hindered internal olefinic carbon leads to the corresponding primary-alkyl palladium species, which leads to methyl ketone. The oxidation pathway most likely occurs by  $\beta$ -hydrogen migration followed by further attack on the coordinated vinyl ether by water (as a trace contaminant in the Bu<sup>t</sup>OH which is then regenerated from Pd<sup>0</sup> by CuCl<sub>2</sub>–O<sub>2</sub>–HCl in the usual way). Alternatively, a *tert*-butyl acetal might be formed which is subsequently hydrolysed.

Evidence for this mechanism is as follows: (i) there is a first-order dependence of the initial rate of aldehyde formation on the Bu<sup>t</sup>OH concentration in dimethylformamide (DMF) solvent; (ii) the use of *n*-butanol or *sec*-butyl alcohol leads to ketal and acetal products, although those derived from *sec*-butyl alcohol readily decompose to the ketone and aldehyde under the reaction conditions;<sup>8</sup> (iii) the selectivity for aldehyde increases as: *n*-butanol < *sec*-butyl alcohol < Bu<sup>t</sup>OH; (iv) small amounts of water increase the rate, but decrease aldehyde selectivity probably owing to competing

**Scheme 1****Scheme 2**

attack by water on the coordinated olefin; and (v) non-protic solvents such as THF and DMF give much lower rates and aldehyde selectivities (Table 1).

One of the more intriguing aspects of this system is that the oxidation reaction can be switched on or off depending on whether oxygen is present, whereas the exchange reaction remains unaffected. Fig. 1 demonstrates this for the oxidation and exchange of allyl ethyl ether, which is much more prone to exchange than allyl acetate. Therefore, the Pd<sup>II</sup> is still present and active under nitrogen, but it will not oxidize the olefin until oxygen is added. This runs counter to the accepted role of copper and oxygen in the Wacker system, which is to simply re-oxidize Pd<sup>0</sup>. Therefore, this might offer some insight into the role of Cu and O<sub>2</sub> in the Wacker reaction, which has long been debated.<sup>9</sup>

Along these lines, we have undertaken some initial studies to probe the mechanism of the switching between exchange and oxidation. Palladium salts by themselves are known to catalyse allylic exchange and we have demonstrated this with our system. However, some HCl is required to prevent spontaneous reduction of the palladium. § Adding oxygen has

§ Efficient exchange of the allylic substituents in the absence of oxygen occurs only if CuCl<sub>2</sub> is present—it is likely that the CuCl<sub>2</sub> only serves to regenerate Pd<sup>II</sup>, which liberates HCl upon reduction to Pd<sup>0</sup>.

no effect on the system in the absence of copper, thereby ruling out a Pd-OOH intermediate.<sup>10</sup> Therefore, both copper and oxygen are involved, but the oxidation state of copper is very important. In catalytic oxidation reactions, a significant induction period is observed when CuCl<sub>2</sub> is substituted for CuCl. This could be explained in two ways: (i) the CuCl serves as an HCl scavenger in the presence of oxygen and, therefore, drives the oxidation reaction, or (ii) a copper-oxygen complex is formed which oxidizes palladium intermediate **1** and initiates the oxidation route.<sup>11</sup> Our current evidence is insufficient to distinguish among these possibilities. However, *tert*-butyl nitrite, especially in the presence of oxygen, also switches on the oxidation pathway which supports the role of Cu/O<sub>2</sub> as an oxidant. Further studies are underway to better elucidate the true roles of copper and oxygen in this system.

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