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**PALLADIUM CATALYZED INDIRECT ELECTROCHEMICAL
ACETOXYLATION OF OLEFINS**

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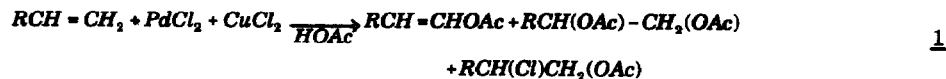
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Summary: *Olefins are acetoxyated to allylic and vinylic unsaturated esters by palladium (II) acetate catalyst in combination with controlled current anodic reoxidation and copper (II) acetate as an electron transfer agent.*

Considerable effort has been devoted to the study of the acetoxylation of olefins^{1,2} since the original report by Moiseev and co-workers of the oxidation of olefins by palladium (II) salts in acetic acid.³ Originally, it was thought that vinyl acetate could be produced commercially by this homogenous process. However, serious product selectivity and corrosion problems have prevented this. The palladium catalyst promotes this conversion stoichiometrically, and (similar to other Wacker-type processes), for every turnover, active Pd(II) is reduced to inactive Pd(0). In order to obtain a fully catalytic system appropriate reoxidants must be used to regenerate Pd(II). A variety of species have been used for this purpose, including FeCl₃, TiCl₃, AuCl₄⁻ and, most notably CuCl₂.¹ This regeneration functions by, for example, using CuCl₂ to reoxidize Pd(0) back to Pd(II) *in situ*, and air to reoxidize CuCl back to CuCl₂.

The distribution of products for the oxidation of olefins in acetic acid can be very complex. In and of itself, isomerization of the oxypalladation intermediate can lead to mixtures of allylic and vinylic unsaturated products. However, the presence of chemical reoxidants such as copper can have dramatic effects on product selectivity - particularly when chloro ligands are present. Reoxidants such as CuCl₂, while enhancing the rate of reaction, do produce substantial quantities of saturated 1,2-disubstituted

esters⁴ (eq.1). Even low concentrations of CuCl_2 can result in as high as a 40:1 saturated/unsaturated product ratio.⁵

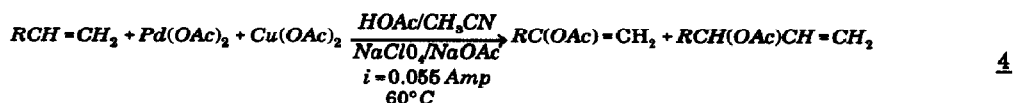


Recently we published several reports^{6,7} describing the electrochemical reoxidation of palladium(II) chloride in Wacker-type oxidative carbonylation of olefins and alkynes (eq. 2,3)



This type of catalysis in effect functions as a pseudo-heterogeneous system, yet is quite selective under very mild (1atm, $\leq 50^\circ\text{C}$) reaction conditions. Catalyst/product separation can be conducted easily by simply reversing the voltage and electroplating the catalyst out onto the electrode. Thus, this technique combines some of the best features of homogenous and heterogenous catalysis — namely, high product selectivity coupled with facile catalyst/product separation. This method also proved to be very convenient for regenerating spent palladium catalyst in situ.

This work prompted an attempt to electrochemically regenerate Pd(II) for olefin acetoxylation in the absence of chloride salts. When olefins are reacted with palladium (II) acetate, allylic and vinylic unsaturated mono-esters products are formed in fair to excellent current efficiency (eq. 4).



While palladium (II) acetate converts the olefin to unsaturated ester, the copper (II) acetate

functions as a homogeneous electron transfer agent to help regenerate spent palladium catalyst (Figure 1).

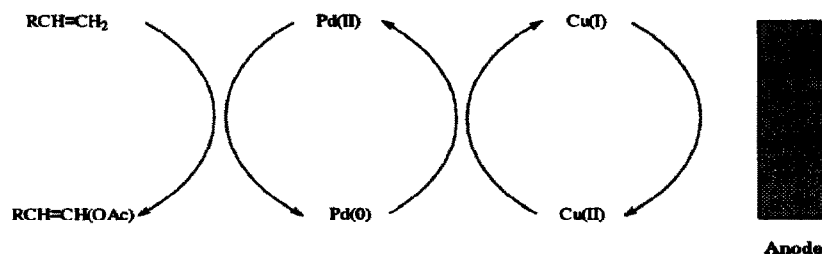


Figure 1

The experimental results (Table I) reveal that this system works quite well for alpha olefins and produces unsaturated acetoxy derivatives cleanly, with good current efficiencies. Current efficiency generally improved with increasing chain length. Not surprisingly, functionalized olefins with bulky side-groups (such as phenyl) convert with only fair current efficiencies.

Table I Pd(OAc)₂ Catalyzed Acetoxylation of Olefins

Substrates	Current Efficiency ^a
1-Decene	91%
1-Octene	83%
1-Heptene	64%
Styrene	35%
Vinylcyclohexane	33%
Cycloheptene	72% ^b
Cyclohexene	29% ^c

^a Current efficiency and yields are based upon disappearance of olefin starting material. No substances other than olefin substrates and ester products were detected. An internal standard method was used with GC analysis to calculate the yield and hence the current efficiency. For convenience, each reaction was run until 1/2 equivalent of electricity had been consumed. Thus reaction yield = 1/2 (current efficiency) for all entries in Table I. (These reactions, however, can be pushed to completion simply by input of more electricity).

^b Ratio allylic/vinylic product: 13/1. Determined from proton NMR.

^c Ratio allylic/vinylic product: 1/1. Determined from proton NMR.

The results for cyclic olefins proved variable. Acetoxylation of cycloheptene afforded unsaturated ester products with a current efficiency of 72%. However, >90% of the product was allylic ester and <10% was vinylic ester. On the other hand, acetoxylation of cyclohexene produced unsaturated ester products with much less current efficiency (29%) and in a 50:50 mixture of allylic and vinylic products.

The following general procedure was used: a 1/1 solution of acetic acid and acetonitrile totalling about 150 ml was prepared. To this was added sufficient sodium perchlorate and sodium acetate to make the solution 0.1 M in each. This solution was introduced to a divided cell and placed under an inert atmosphere. Graphite felt electrodes (Electrosynthesis Co., type GFS6 (ca. 2 x 5 x 0.5 cm)) were inserted into the reactor as well as a saturated calomel reference electrode. Then Pd(OAc)₂ (0.5 mmol), Cu(OAc)₂ (1.0 mmol), and substrate (10.0 mmol) were added in sequence. The reaction was run at 60°C at a controlled current of $i = 0.055$ Amp until 1/2 equivalent of electricity had been consumed. Work-up consisted of extraction into hexane and purification by column chromatography. Analyses were conducted using NMR, GC and GC/MS.

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