The Mechanism of the Palladium-catalysed Reaction of Allylic Acetates with Carbonyl Compounds *via* Electrochemical Reduction

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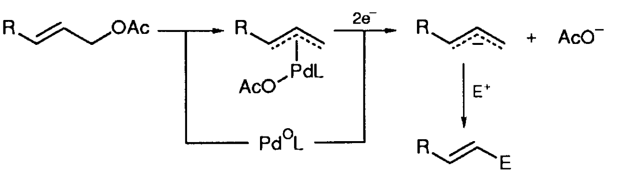
The mechanism of Pd-catalysed reaction of allylic acetates with carbonyl compounds in the presence of zinc chloride *via* electroreduction is reported.

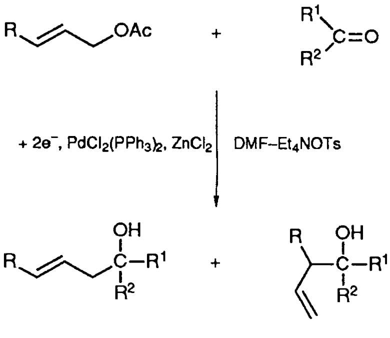
The Pd-catalysed electroreductive cleavage of allylic acetates has been reported[1] to provide allylic carbanions, which could be easily captured by H^+ or Me_3SiCl (Scheme 1). The allylic carbanions formed under these conditions were probably too reactive for nucleophilic reaction with carbonyl compounds, as this paper made no mention of C–C bond formation. Subsequently it was reported[2] that in the presence of zinc chloride under the above mentioned conditions, the displacement of allylic compounds with carbonyl compounds took place and fairly good yields of corresponding homoallylic alcohols were obtained (Scheme 2). It was suggested that zinc chloride might act as a Lewis acid and the intermediate allylic carbanions might be stabilized by forming an allylic zinc reagent. No details of the mechanism were given. In this paper we report our electrochemical results which are relevant to the mechanism.



$E^+ = H^+$ or Me_3Si^+

Scheme 1

To study the mechanism, benzaldehyde was used as a model carbonyl compound. By using the potential sweep method, we revealed the following. (*i*) Both allyl acetate and benzaldehyde showed no reduction peak in 0.1 mol dm^{-3} Et_4NOTs–DMF† solution (Fig. 1*a*). (*ii*) A reduction peak at −0.87 V (*vs.* SCE† throughout) in a 0.1 mol dm^{-3} Et_4NOTs–DMF solution



Scheme 2

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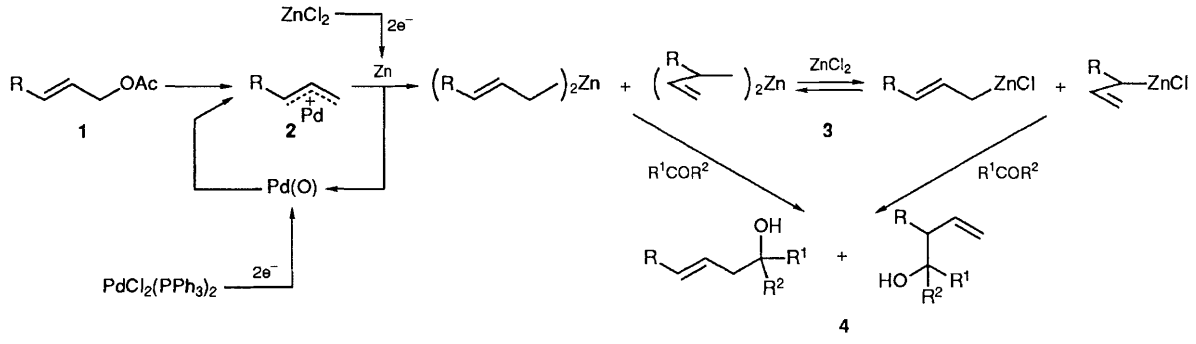
† Abbreviations used: Ts = p-$MeC_6H_4SO_2$; DMF = dimethylformamide; SCE = saturated calomel electrode.



Scheme 3

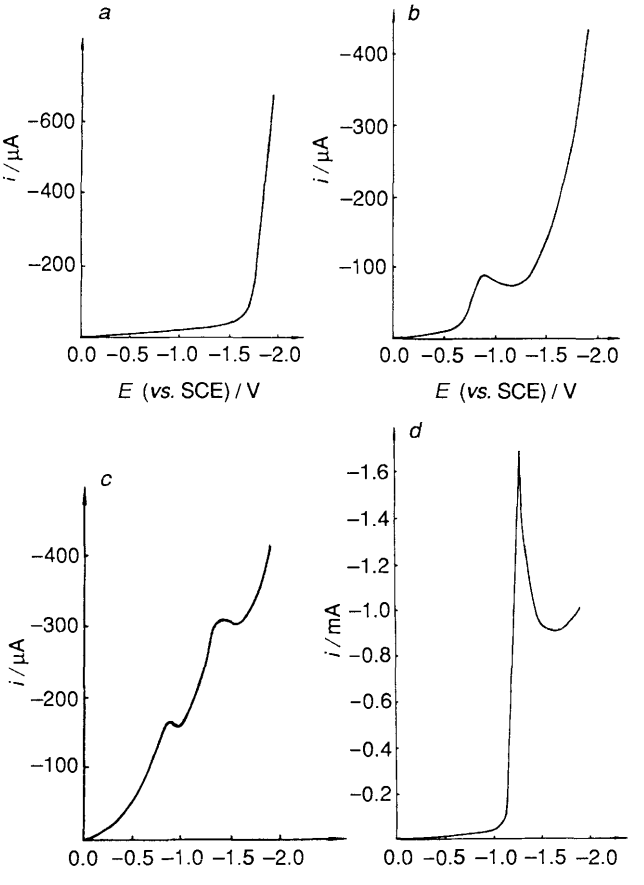


Fig. 1 Voltammograms recorded at 20 mV s^{-1} of: (*a*) 0.044 mol dm^{-3} $CH_2{=}CHCH_2OAc$ (0.05 mol dm^{-3} PhCHO) in 0.1 mol dm^{-3} Et_4NOTs–DMF; (*b*) 6.6 × 10^{-3} mol dm^{-3} $PdCl_2(PPh_3)$ in 0.1 mol dm^{-3} Et_4NOTs–DMF; (*c*) 0.05 mol dm^{-3} $CH_2{=}CHCH_2$ OAc and 6.6 × 10^{-3} mol dm^{-3} $PdCl_2(PPh_3)_2$ in 0.1 mol dm^{-3} Et_4NOTs–DMF and (*d*) 0.2 mol dm^{-3} $ZnCl_2$ in 0.1 mol dm^{-3} Et_4NOTs–DMF

of $PdCl_2(PPh_3)_2$ indicated its reduction to a Pd^0 complex (Fig. 1*b*). (*iii*) Addition of allyl acetate to a solution of $PdCl_2(PPh_3)_2$ in 0.1 mol dm^{-3} Et_4NOTs–DMF, resulted in a reduction peak at −1.35 V (Fig. 1*c*), in addition to the peak at −0.87 V. This peak at −1.35 V indicated that the allylic carbanion had been formed through the reduction of the intermediate π-allylic palladium complex. (*iv*) The reduction peak of $ZnCl_2$ in 0.1 mol dm^{-3} Et_4NOTs–DMF solution occurs at −1.24 V (Fig. 1*d*). Thus, under the experimental conditions used the reduction of $ZnCl_2$ was easier than that of π-allylic palladium.

Masuyama *et al.*[3] reported that in the presence of zinc powder and a catalytic amount of Pd^0 compounds allylic acetates reacted with carbonyl compounds in dioxane producing homoallylic alcohols in reasonable yields. Therefore, zinc metal might be the real reducing agent in the Pd-catalysed allylation of carbonyl compounds *via* electrochemical reduction. In order to prove this, constant potential electrolysis at −1.30 V was performed in an H-type divided cell fitted with Pt electrodes.‡ After usual work-up 72% of homoallylic alcohol was obtained. Masuyama *et al.*[3] found that the yields of homoallylic alcohols were very low when the reaction was carried out in DMF. The zinc formed *in situ* in our work should be more reactive than the zinc powder used by Masuyama *et al.*[3]

The same results would be expected in the Pd-catalysed allylation of carbonyl compounds if a catalytic amount of the Pd^0–allylic acetate complex prepared beforehand was used instead of $PdCl_2(PPh_3)_2$. However, no homoallylic alcohol could be isolated from the electrolyte even if the potential applied reached −1.45 V if the reduction was carried out without zinc chloride or Pd^0.

Based on the above results, we propose the following mechanism for the Pd-catalysed reaction of allylic acetates with carbonyl compounds *via* electroreduction (Scheme 3). Addition of allylic acetate **1** to the Pd^0 complex generated from electroreduction of $PdCl_2(PPh_3)_2$ gives the Pd^0–allylic acetate complex **2**. Complex **2** is then transformed to the diallylzinc complex *via* reaction with the nascent zinc, formed by electroreduction of zinc chloride. Because a large excess of zinc chloride was present in the electrolyte an equilibrium between diallylzinc and allylzinc chloride **3** could exist.[4] Both diallylzinc and allylzinc chloride would react with carbonyl compounds forming the homoallylic alcohols **4**.

Finally, using electrochemical techniques we showed that the reduction of $PdCl_2(PPh_3)_2$ was irreversible and was charge-transfer controlled. The n value of the charge-transfer step was 2, and i^0 and transfer coefficient (α) values were 5.67 × 10^{-8} A and 0.15 respectively. We also determined that the reduction of $ZnCl_2$ in DMF was diffusion charge-transfer controlled.

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‡ A DMF solution of Et_4NOTs (0.5 g in 10 ml), $ZnCl_2$(1 g in 10 ml), allyl acetate (3.4 mmol), benzaldehyde (1.6 mmol) and $PdCl_2(PPh_3)_2$ (100 mg) was placed in the cathode chamber and a DMF solution of Et_4NOTs (0.5g in 10ml) in the anode chamber. At room temperature, under nitrogen and with continuous stirring, a constant potential of −1.30 V was applied until most of the starting material had been consumed (5 F mol^{-1}). After usual work-up 72% of homoallyl alcohol was obtained.