Palladium(II) Catalysed Synthesis of Allylic Esters

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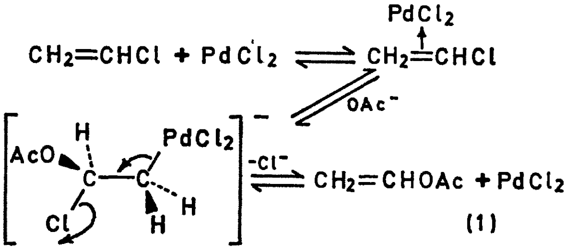
Summary The displacement of chloride ion from allylic centres by acetate ion is markedly catalysed by palladium(II) chloride.

RECENTLY, the palladium(II) chloride catalysed synthesis of vinyl acetate *via* the reaction of vinyl chloride with acetate ion was reported.[1-3] Deuterium labelling experiments demonstrated that the acetate ion substitutes at the chlorine-carrying carbon atom and that the geometric configuration of the deuteriated vinyl chloride is lost in the vinyl acetate produced. An addition–elimination mechanism was suggested to explain these results (equation 1).[2,3]



(1)

I describe the catalytic participation of palladium chloride in the displacement of chloride ion from allylic centres by acetate ion and the probable involvement of a similar addition–elimination type mechanism. The results of this study (see Table) clearly demonstrate the catalytic activity of palladium chloride and constitute the first well defined evidence for such participation involving displacement from allylic systems.

Reaction of $R^1CH{=}CH{\cdot}C(R^2)HCl$ *with* NaOAc *using* $PdCl_2$ *catalyst*[a]

R^1	R^2	Temp. (°)	Time (hr.)	Catalyst	Conversion (%)[b]
H	H	25	4	No	trace
H	H	25	2·5	Yes	100
Me	H	65	4	No	30[c]
Me	H	65	1	Yes	100[d]
H	Me	65	4·5	No	trace
H	Me	65	1	Yes	97[d]

[a] In a typical experiment freshly distilled allyl chloride (0·12 mole), dry sodium acetate (0·10 mole), and palladium chloride (0·01 mole) were allowed to react under a nitrogen atmosphere in 50 ml of DMF. Disappearance of allyl chloride was followed by g.l.c. The products were purified by distillation and further analysed by i.r. and n.m.r. spectroscopy. No vinylic esters were detected in any of the systems.

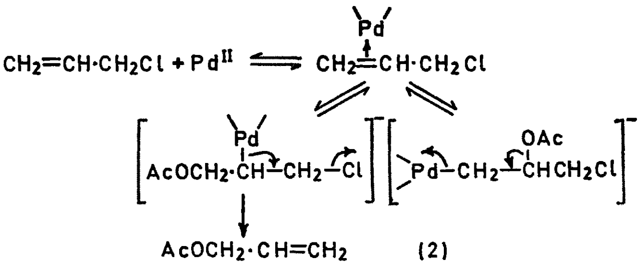
[b] Based on allylic chloride consumed.

[c] Only but-2-enyl acetate was formed.

[d] Two isomeric acetates were formed in the same ratio (*ca.* 65% but-2-enyl acetate, 35% 3-acetoxybut-1-ene).

Since palladium chloride is known to react with allyl chloride under mild conditions to give the corresponding π-allyl complex, the intermediacy of this species either as a catalyst or as a reaction intermediate was of interest. Accordingly, it was shown that pure π-allylpalladium chloride does not react with sodium acetate to give a high yield of allyl acetate and does not serve as a catalyst for the reaction of sodium acetate with allyl chloride. It should also be noted that palladium chloride does not catalyse the reaction of simple alkyl chlorides (1-chloropentane, benzyl chloride) with sodium acetate under the conditions given in the Table.

These results indicate that an addition–elimination mechanism is involved (equation 2). If this is so then the products should be those expected from an overall S_N2' type process. Unfortunately, the butenyl chlorides did not allow proof of this due to competing side reactions involving rapid equilibration of both starting materials as well as products.



(2)

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[1] E. W. Stern, M. L. Spector, and H. P. Leftin, *J. Catalysis*, 1966, **6**, 152.

[2] C. F. Kohll and R. Van Helden, *Rec. Trav. chim.*, 1968, **87**, 481.

[3] H. C. Volger, *Rec. Trav. chim.*, 1968, **87**, 501.