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METAL π-ALLYL CHEMISTRY

II*. THE ALKALINE HYDROLYSIS OF π-ALLYLPALLADIUM CHLORIDE

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SUMMARY

Investigation of the alkaline hydrolysis of π-allylpalladium chloride in boiling water has shown that when the products are swept out as they are formed using oxygen-free nitrogen the oxygen-containing product of the hydrolysis is acetone. This result, together with earlier reports of acrolein and allyl alcohol as the oxygen-containing hydrolysis products, suggests that the reaction is more complex than previously considered.

INTRODUCTION

Early work on the hydrolysis of π-allylpalladium chloride suggested that the reaction followed a relatively simple path yielding propene and acrolein together with palladium metal (eqn. (1))[1]. Subsequent investigation showed that the majority of the extra hydrogen atoms incorporated in the π-allyl group that is liberated as propene do not come from the solvent[2]. Thus on warming π-allylpalladium chloride with a 0.1 M solution of sodium deuteroxide in D_2O it was found that 83% of the propene liberated was in the undeuterated form. Further, these investigators found that the oxygen-containing product formed simultaneously with the propene was allyl alcohol[2] rather than acrolein as had been found previously. As part of a general investigation of the reactions of π-allylic complexes we set out to investigate the nature of the oxygen-containing product of the hydrolysis of π-allylpalladium chloride. A major difficulty arose when we attempted to reproduce the earlier reaction conditions under which the formation of allyl alcohol had been reported since the authors merely state that π-allylpalladium chloride was "heated" with a 0.1 M aqueous solution of sodium hydroxide[2]. Although the precise temperature at which the complex was heated is not recorded, elsewhere in the paper it is noted that the decomposition reaction occurs at 80°.

$$[(\pi\text{-}C_3H_5)PdCl]_2 + H_2O \rightarrow Pd^0 + CH_2{=}CH{-}CHO + CH_2{=}CH{-}CH_3 + 2HCl \qquad (1)$$

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* For Part I see ref. 9.

EXPERIMENTAL

Preparation of di-μ-chlorodi-π-allyldipalladium(II)

This compound was prepared by treating palladium(II) chloride with allyl chloride in 50% acetic acid at room temperature for 15 h[1]. (Found: Pd, 57.8. $C_6H_{10}Cl_2Pd_2$ calcd.: Pd, 58.3%.) M.p. 154–155° with decomposition (lit.[1] 160° with decomposition). The product existed as brilliant yellow needle-like crystals indicative of the α-form[3] as opposed to the lime green product, which is a mixture of the α- and β-forms[3], obtained using allyl alcohol instead of allyl chloride[4].

Hydrolysis of π-allylpalladium chloride

A solution of π-allylpalladium chloride (0.02 g) in water (20 ml) was boiled gently with sodium hydroxide (2 ml of 0.1 *M*) in a two-necked flask provided with a nitrogen inlet and a reflux condenser through which was passed a very slow stream of water. A very brisk flow of oxygen-free nitrogen was passed into the flask and after leaving the condenser it was passed first into a gas wash-bottle containing a saturated solution of 2,4-dinitrophenylhydrazine hydrochloride in methanol (20 ml), where the 2,4-dinitrophenylhydrazone (DNP) derivative of the carbonyl compound was precipitated, and secondly into a gas wash-bottle containing a dilute aqueous solution of potassium permanganate. The hydrolysis was repeated twelve times.

The hydrolysate DNP derivative was identified as the DNP derivative of acetone as follows. One fraction was recrystallised from methanol and found to melt at 125–126° as compared to acetone DNP (m.p. 127–128°). A mixed authentic acetone-DNP/hydrolysate-DNP sample melted at 126–127° (acrolein DNP[5] melts at 165°). The infrared spectrum of a second fraction of the hydrolysate DNP was recorded in a nujol mull and compared with the infrared spectra of acetone DNP and acrolein DNP. The spectra of the hydrolysate DNP and acetone DNP were identical and showed significant differences in the region 1600–800 cm^{-1} from the acrolein DNP (see Table 1). A third fraction of the crude (unrecrystallised) hydrolysate DNP was analysed using paper chromatography. Using n-heptane saturated with methanol the hydrolysate DNP was found to move at exactly the same rate as the authentic acetone DNP derivative whereas acrolein DNP moved at only 0.45 times this rate. In only one of the twelve runs was any acrolein DNP detected and on that occasion it only amounted to a very small trace. The yield of acetone DNP varied slightly from one run to another but always represented between 30 and 40% of the π-allyl groups initially present.

The propene was determined quantitatively by the decolourisation of potassium permanganate as determined by the decrease in the absorbance at 529 nm measured on a Unicam SP500 spectrophotometer. In a series of hydrolyses it was found that the proportion of the π-allyl groups present in the initial π-allylpalladium chloride that were converted to propene varied slightly from run to run, but were always in the range 60–70%. This is very similar to the 58% reported previously[2]. It is noteworthy that the sum of the acetone and propene yields in each run amounted to virtually 100%. An attempt to correlate the temperature at which the π-allylpalladium chloride was hydrolysed with the ratio of acetone to propene gave inconsistent results suggesting that this was not the factor responsible for the slight fluctuations in this ratio.

TABLE 1

DIFFERENCES IN THE INFRARED SPECTRA OF THE HYDROLYSATE DNP AND ACETONE DNP AS COMPARED WITH ACROLEIN DNP IN THE REGION 1600–800 cm^{-1}

Acetone DNP and hydrolysate DNP	*Acrolein DNP*
1590 s	1598 s
1547 w	1547 m
1470 and 1462 s both peaks equally intense	1470 s, 1462 (w sh)
1390 m	No band at 1390
1265 m	No band at 1265
No band at 1190	1190 m
1135 m	1135 s
1104 m	No band at 1104
No band at 1082	1082 s
1062 s	1059 m
1031 m	1031 (vw sh)
No bands at 1003, 981, 960 or 952	1003 ms, 981 w, 960 m, 952 m
915 m, 858 m s	No bands at 915 or 858

DISCUSSION

The observation of acetone as the principal hydrolysis product of π-allylpalladium chloride has not previously been reported. We therefore took elaborate precautions to ensure that it had not been introduced accidentally into the apparatus during cleaning after a previous experiment, by thoroughly rinsing the apparatus with methanol and drying it in an oven at 110° for at least an hour before each experiment. The π-allylpalladium chloride complex was thoroughly dried for 24 h in a continuously pumped vacuum pistol, and the absence of acetone checked by proton NMR.

Because of the lack of a detailed description of the conditions it is difficult to compare the present results with those of Schenach and Caserio[2]. However, they can be compared with those of Hüttel *et al.*[1]. In Hüttel's experiment π-allylpalladium chloride was boiled for two hours under reflux in water (not sodium hydroxide, although Hüttel does state that in 0.1 *M* sodium hydroxide the results are the same) and the palladium metal that was deposited was filtered off before the distillation. In the present case the distillation took place in the presence of palladium metal. This could conceivably be responsible for the formation of acetone rather than acrolein since palladium metal is known to catalyse the hydrogenation and isomerisation of olefins[6]. However, the palladium-catalysed conversion of acrolein to acetone under the present conditions seems very unlikely particularly as Hüttel had palladium present during the refluxing for two hours, which should have been sufficient time for it to effect such a conversion if that were possible.

The observation of acetone in the present work, and acrolein[1] and allyl alcohol[2] previously, indicates that the hydrolysis of π-allylpalladium chloride is more complex and susceptible to changes in the reaction conditions than previously considered. It would be premature to speculate on a possible mechanism for the formation of acetone and propene during the alkaline hydrolysis of π-allylpalladium chloride, and we are currently investigating the reaction in more detail. However, it may be significant that propene undergoes oxidative hydrolysis in the presence of palladium(II) salts, although not in the presence of palladium metal, to yield acetone[7]. This may be related to the relationship between the amounts of propene and acetone formed. It is noteworthy that the oxidation of propene by mercuric salts yields acrolein, acetone, traces of allyl alcohol and propanol in a reaction that is considered to involve the initial formation of a π-allylmercury(II) complex[8].

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