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PdCl π-ALLYL COMPLEXING BY SOME 3-OXO-$\Delta^{4,5}$-STEROIDS

R.W. Howsam and F.J. McQuillin

School of Chemistry, The University of Newcastle upon Tyne.

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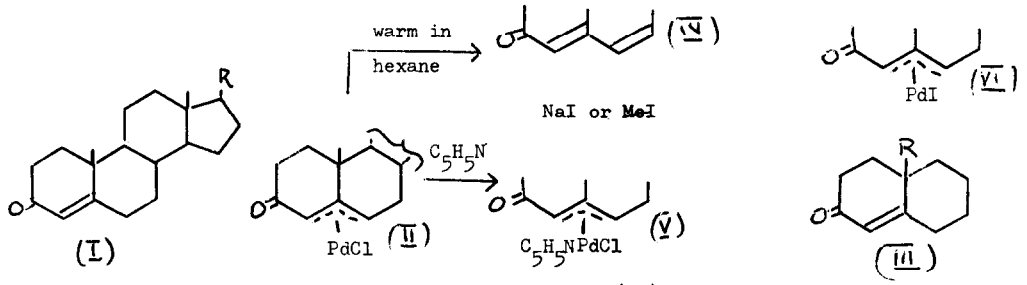
As a parallel with the process of chemisorption in catalysis (1) we have examined the interaction of a group of 3-oxo-$\Delta^{4,5}$-steroids (I) with $PdCl_2$ derivatives. Reaction with Na_2PdCl_4, $(PhCN)_2\ PdCl_2$ or $(C_2H_4\ PdCl_2)_2$ gave PdCl π-allyl complexes of type (II), and analogous products were obtained from (III, R = Me, or CO_2Et). These derivatives correspond with the known PdCl π-allyl complex from mesityl oxide (2).



Steroid (I)	λ 244 mμ	Complex (II) λ 282 mμ	$[\alpha]_D$
R = β-C_8H_{17}	6370	7360	162°
β-OH	6120	6720	218
β-OH, α-Me	6120	6690	204
O =	7360	8240	364
β-COMe	6860	7750	348
CH_2=	5780	6025	369
III, R = Me	9270	9000*	-
III, R = CO_2Et	12,210	16,560*	-

* λ_{max} 275 mμ

The PdCl-derivatives (II), purified by T.L.C. on silica gel gave analytical data in excellent agreement with the formulation(II), and molecular weights in chloroform corresponding to partially dissociated dimers. In the complexes the 4.5 τ vinyl proton signal of the enone (I) was replaced by two one proton signals at 5.6 and 6.6 τ. The complexes showed $\nu_{C=O}$ 1680 cm.$^{-1}$ as in the parent (I), but the related $\nu_{C=C}$ at 1610 cm.$^{-1}$ was absent. In the ultraviolet the 240 mμ enone adsorption was replaced in the complex by two bands at 244 and 282 mμ of lower intensity.

As expected $\Delta^{4,5}$- and $\Delta^{5,6}$-cholesten-3-one gave the same derivative. 17-Methyltestosterone gave two products, (II, R = β-OH, α-Me) accompanied by a second complex, (II, R = CH_2=) which could be obtained more directly from the dehydration product from 17-methyl testosterone. With $(PhCN)_2PdCl_2$ in $CDCl_3$ testosterone showed progressive displacement of the 17-hydroxyl proton signal at 8.03 τ to 7.13 τ which could be removed by shaking with D_2O. The dehydration of 17-methyl testosterone under very mild conditions presumably arises from an interaction of this kind with the hydroxyl group.

Various chemical transformations of the cholestenone complex (II, R = β-C_8H_{17}) are summarised below. The pyridine complex (V), and the iodo-derivative (VI) were isolated and analysed. The interesting halogen exchange on warming the complex in methyl iodide is most easily rationalised in terms of an intermediate methyl iodide adduct; methylation of the steroid was not observed. The complex, shaken with hydrogen in methanol, gave 5αH- and 5βH-cholestan-3-one in closely equal amounts. From deuterium in CH_3OD the product contained up to 4D atoms/mol., of which two were retained after equilibration in CH_3OH. With $SnCl_2$ in methanol the complex gave a red derivative which when shaken in hydrogen reformed cholest-4-en-3-one; $SnCl_2$ is a known hydrogenation inhibitor. The ready decomposition to give the dienone (IV) constitutes a novel dehydrogenation reaction.

Establishing the stereochemistry of the complexes must await X-ray structure analysis. The generally positive rotational change on complexing suggests, however, a common stereochemistry of co-ordination throughout the group.

References

1. Cf. I. Jardine and F.J. McQuillin, J.Chem.Soc.,(C), 1966, 458.

2. G.W. Parshall and G. Wilkinson, Inorg. Chem., 1962, 1, 896.