Palladium Chloride–π-Allyl Complexes from Calciferol and Related Compounds

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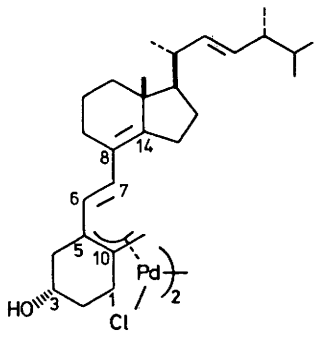
Summary π-Allyl complexes of palladium have been prepared from calciferol, ergosterol, 3-*epi*-ergosterol, and 7-dehydrocholesterol; in contrast, cholesterol afforded cholesteryl chloride under similar conditions.

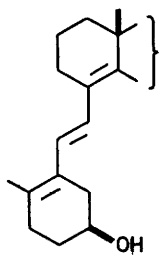
π-ALLYL complexes have become important in organic synthesis,[1] because of their reactivity with nucleophiles[2] and because of their oxidisability to allylic alcohols.[3] In principle, π-allyl complexes could be useful in modifying the functionality of biologically active vitamin D analogues.[4] We report here the formation of such complexes from steroids of biological importance.

Treatment of calciferol with bis(benzonitrile)palladium dichloride (1 equiv.) in $CHCl_3$ or acetone (with or without inorganic bases) at room temperature readily gave a dimeric (osmometry) yellow complex, m.p. 170—172 °C, $[\alpha]_D$ + 186° (c = 0·156 in $CHCl_3$), in *ca.* 70% yield. This complex is formulated as (**1**) on the basis of elemental analysis, molecular weight determination, and the following considerations. In the n.m.r. spectrum the C-19 protons were shifted upfield and the C-18 protons downfield in agreement[5] with the structure (**1**). Reduction of the complex with lithium hydridotri(t-butoxy)aluminate gave smoothly the known[6] isotachysterol$_2$ (**2**). ^{13}C N.m.r. measurements on complex (**1**) showed[7] an upfield shift for C-5 ($\Delta\delta$ 78 p.p.m.) and C-19 ($\Delta\delta$ 59 p.p.m.) compared to C-10. In addition C-14 appeared as a vinyl carbon at low field. The assignment of the α-sterochemistry to complex (**1**) is by analogy (complexing on same side as the hydroxy group) with our work on iron carbonyl complexation.[5]

When ergosterol was palladised under the same conditions it afforded, in 1 h, a yellow dimer, m.p. 153—155 °C, $[\alpha]_D$ + 2170° (c = 0·159 in $CHCl_3$), in 62% yield, to which



(1)



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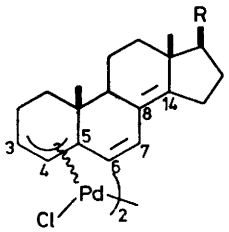

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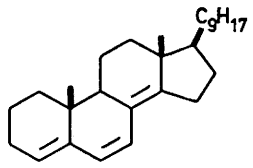

(4)

a; R = C_9H_{17}
b; R = C_8H_{17}

structure (**3a**) was assigned on the basis of elemental analysis, osmometry (dimer), lack of hydroxy group, and ^1H n.m.r. (six vinyl protons) spectroscopy. Reduction of (**3a**) with lithium hydridotri(t-butoxy)aluminate afforded,

in high yield, the known[8] tetraene (**4**) which is in agreement with the proposed structure.

For comparison of n.m.r. spectra, the corresponding complex (**3b**) (69%), m.p. 154—156 °C, $[\alpha]_D$ + 2220° (c = 0·154 in $CHCl_3$) of 7-dehydrocholesterol was also prepared. This compound showed H-6 and H-7 at 6·83 and 5·60 with J 9 Hz as well as a doublet for H-4 (δ 5·26, J 6 Hz) and a multiplet for H-3 at δ 4·88. For both (**3a**) and (**3b**) a downfield shift of the C-18 protons confirmed unsaturation in ring c. ^{13}C N.m.r. measurements showed an upfield shift for C-3, C-4, and C-5 involved in the complex.

3-*epi*-Ergosterol[5] gave the same complex (83%) as ergosterol in a markedly faster reaction (a few minutes).

With these data at hand it is possible to be certain of the constitution of compounds (**3a**) and (**3b**) but not of the configuration of the palladium residue.

In contrast, cholesterol, when palladated as above, gave no reaction. On warming, palladium metal was deposited and a high yield of cholesterol chloride was obtained.

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