Structure and Chemistry of π-Allyl Palladium Complexes from Steroids

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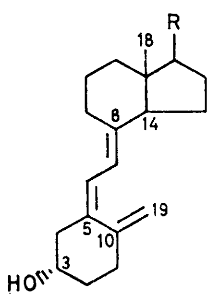
The synthesis and structures of π-allyl palladium complexes prepared from vitamins D_2 and D_3 and from ergosterol, 7,8-didehydrocholesterol, and 3-*epi*-cholesterol are described. The mechanism of palladisation is discussed as well as the transformation of the complexes into conjugated trienes or allylic alcohols.

DURING the course of our investigations on the use of organometallic complexes as protecting groups or as reactive intermediates we have studied complexation of steroids of biological importance.[1] Attention was also given [2] to the chemistry of Pd^{II}, which has become important in organic synthesis [3] for its ability to activate a methylene group α to an unsaturated group and because the π-allyl complex reacts readily with nucleophiles. In principle π-allyl complexes could be useful in modifying the functionality of biologically active vitamin D analogues.[4] We report here the synthesis and properties of palladium complexes of such compounds the structures of which have been determined by ^{13}C and ^{1}H n.m.r. spectroscopy as well as by chemical means.

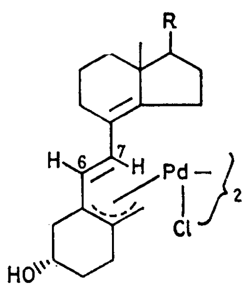
$(PhCN)_2PdCl_2$

(1)



(2)

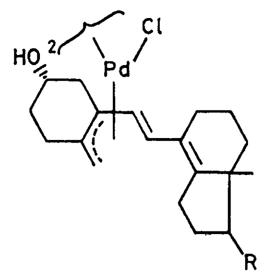
a; $R = C_9H_{17}$
b; $R = C_8H_{17}$



(3)

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

The synthesis of π-allyl palladium complexes can be accomplished by reaction of olefins with $PdCl_4^{2-}$, by exchange with $(C_2H_4)_2PdCl_2$, or more conveniently in our case by addition of bis(benzonitrile)palladium dichloride (1) to the olefin in chloroform or acetone. Thus addition of an equimolar amount of (1) to a solution of calciferol (2a) or cholecalciferol (2b) affords within one hour an almost quantitative yield of complexes (3a) or (3b). These complexes showed the i.r. absorptions due to the OH group but important modification of the >C=C< region compared with the starting material. From elemental analysis, molecular weight determination



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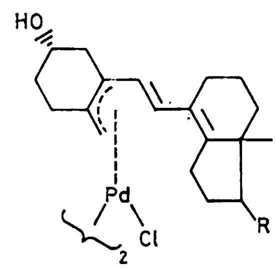

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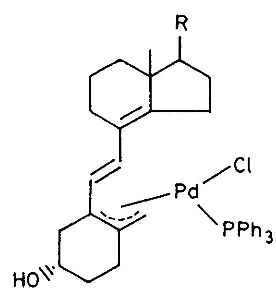

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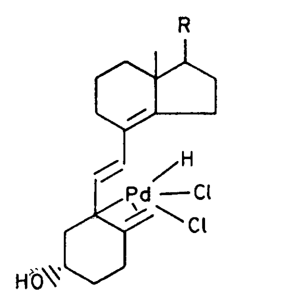


(7)

(osmometry), and other spectroscopic information, formula (3) involving complexation at C(19), C(10), and C(5) with formation of an extra double bond at C(8)–C(14) has been established. The ^{1}H n.m.r. data listed

TABLE 1

^{1}H N.m.r. data (δ values) for compounds (2a), (3a), and (3b)

Compound	$18-H_3$	$19-H_2$	22- and 23-H	6-H	7-H	3-H
(2a)	0.55	6.02	5.13	4.85 (d)	4.86 (d)	3.88
(3a)	0.90	3.23 and 3.60	5.22	5.09 [a] (d)	6.74 (d, *J* 16 Hz)	4.28
(3b)	0.90	3.22 and 3.62		5.12 (d, *J* 16 Hz)	6.75 (d, *J* 16 Hz)	4.28

[a] This signal is partly obscured by the 22- and 23-H resonances.

TABLE 2

^{13}C N.m.r. data (δ values) for compounds (2a), (3a), and (3b) [a]

	C-10	C-5	C-22	C-8	C-23	C-6	C-7	C-19	C-3	C-13	C-14
(2a)	145.1 (s)	142.2 (s)	135.6 (d)	135.1 (s)	132.0 (d)	122.4 (d)	117.6 (d)	112.4 (t)	69.2 (d)		
(3a)	117.9 (s) 116.6 (s)	92.6 (s) 90.0 (s)	135.5 (d)	125.4 (s)	132.5 (d)	121.2 (d)	129.7 (d)	56.2 (t) 53.2 (t)	66.1 (d) 64.8 (d)	44.3 (s)	152.7 (s) 152.5 (s)
(3b)	117.9 (s) 116.8 (s)	92.4 (s) 90.0 (s)		125.3 (s)		121.2 (d)	129.8 (d)	56.2 (t) 53.0 (t)	66.0 (d) 64.7 (d)	44.4 (s)	152.7 (s) 152.5 (s)

[a] δ Values in p.p.m., with multiplicity in parentheses (off-resonance technique); tetrasubstituted carbon atoms C-10, -5, -8, -13 and -14 were identified by low noise.

TABLE 3

^{1}H N.m.r. data for compound (8a) and the complexes (9a) and (9b)

Compound	18-H_3	3-H	4-H	6-H	7-H	22- and 23-H
(8a)	0.65	3.73		5.66	5.46	5.30
(9a)	0.82	4.85 (m)	5.30 [a]	5.60 (d, *J* 10 Hz)	6.83 (d, *J* 10 Hz)	5.30
(9b)	0.82	4.88 (m)	5.26 (d, *J* 6 Hz)	5.60 (d, *J* 10 Hz)	6.83 (d, *J* 10 Hz)	

[a] This signal is partly obscured by the 22- and 23-H resonances.

in Table 1 show a considerable upfield shift for the C(19) protons in agreement with complexation at that position [5] and there is a difference of 0.4 p.p.m. between the two hydrogen resonances. In contrast, 7-H is noticably deshielded compared with 6-H located α to the π-allyl complex and the coupling constant (*J* 16 Hz) shows that there is a *trans*-relationship between these two hydrogen atoms. The downfield shift of 13-Me agrees with the existence of unsaturation in ring C and this is confirmed by ^{13}C n.m.r. data (Table 2) which show a resonance at 152 p.p.m. due to an extra sp^2 carbon atom bearing no hydrogen. Structure (3) is also confirmed by the data in Table 2 showing upfield shifts of 28 p.p.m. for C(10), the central carbon atom of the π-allyl, and of more than 50 p.p.m. for C(19) and C(5). Both the shielding and the values are in the range of data previously reported for exocyclic palladium complexes.[6] This has been interpreted theoretically by selective back-donation from a filled metal orbital to an antibonding orbital of the ligand returning electron density only to the terminal carbon atoms of the π-allyl ligand. However, this ^{13}C n.m.r. study shows also that the signals due to C(3), C(19), C(5), C(10), and C(14) are resolved into two peaks of intensity ratio *ca.* 1 : 1, whose shape and position does not depend on the recording conditions.

This observation is explained by the complicated stereochemistry of the dimers which we regard as a mixture of α- and β-complexes (4) and (5) (*cf.* ref. 1). It is reasonable to assume that complexation on the α- or the β-face of the molecule is responsible for these chemical shift variations. There is already good precedent for complexation on both faces of the vitamin D_2 molecule.[1]

We have tried to separate the two complexes. We prepared the monomers (6) by breaking the metal–chlorine bridge by means of triphenylphosphine. Unfortunately, all attempts to separate the α- and β-complexes have been unsuccessful and the ^{13}C n.m.r. spectra of the mixture show the same pattern as above with additional coupling due to the phosphorus nucleus and only limited variation in chemical shifts.

The formation of the dimers (3) can be rationalised by assuming that complexation occurs primarily at the C(19)–C(10) double bond and that the existence of another *cis*-unsaturation at C(5)–C(6) gives rise to a diene-$PdCl_2$ complex as in the case of cyclo-octadiene.[7] The formation of the intermediate species (7) with a localized double bond is facilitated by the well known propensity for elimination of 14-H. Dehydrohalogenation to give the dimeric species (3) does not imply any stereochemical requirement and would normally lead to a mixture of α- and β-complexes in the dimer.

Although several cholestenes and cholestenones have been palladised previously,[8,9] no attempt has been made to complex ergosterol, the steroidal precursor of vitamin D_2. Addition of (1) to a solution of ergosterol (8a) or 7,8-didehydrocholesterol (8b) afforded, after chromatography, a 55—60% yield of brown, non-polar complexes (9a) and (9b) respectively, which were shown by elemental analysis and osmometry to be dimeric and by i.r. spectroscopy to have lost the 3β-hydroxy-group.

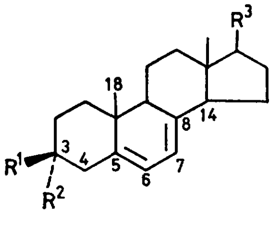
TABLE 4

^{13}C N.m.r. data for the complexes (9a) and (9b) and compound (12) [a]

	C-14	C-22	C-23	C-7	C-6	C-8	C-5	C-4	C-3
(9a)	152.3 (s)	135.4 (d)	132.4 (d)	129.9 (d)	127.4 (d)	125.7 (s)	103.7 (s)	96.7 (d)	75.6 (d)
(9b)	152.5 (s)			129.9 (d)	127.2 (d)	125.5 (s)	103.8 (s)	96.7 (d)	75.6 (d)
(12c)	148.1 (s)	135.4 (d)	132.1 (d)	126 8 (d)	123.6 (d)	125.2 (s)	143.2 (s)	123.6 (d)	

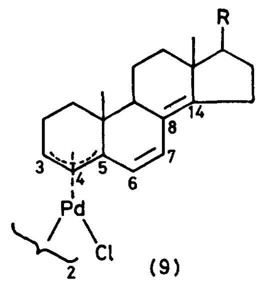
[a] δ Values in p.p.m. with multiplicity in parentheses (off-resonance technique); tetrasubstituted carbon atoms C-5, -8, and -14 were identified by low noise.

Formula (9) has been established on the basis of ^{1}H and ^{13}C n.m.r. data (Tables 3 and 4). Chemical shifts for 3- and 4-H and C(4), C(5), and C(7) are in agreement with data published for endocyclic π-allyl palladium com-



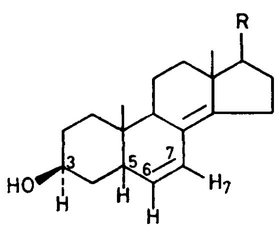
(8)

a; $R^1 = OH$, $R^2 = H$, $R^3 = C_9H_{17}$
b; $R^1 = OH$, $R^2 = H$, $R^3 = C_8H_{17}$
c; $R^1 = H$, $R^2 = OH$, $R^3 = C_9H_{17}$



(9)

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



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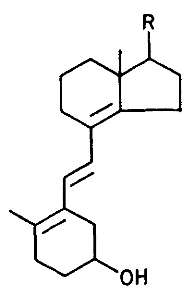
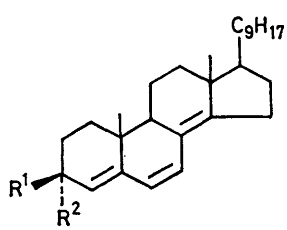


(11) $R = C_9H_{17}$



(12)

a; $R^1 = H$, $R^2 = OH$
b; $R^1 = OH$, $R^2 = H$
c; $R^1 = R^2 = H$

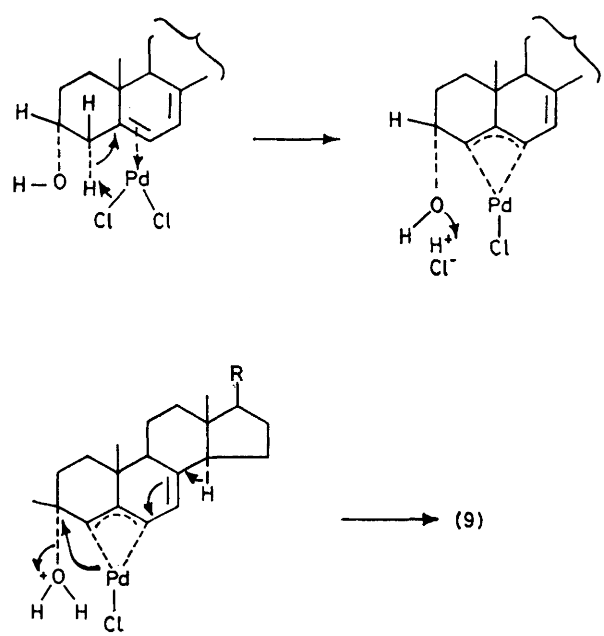
plexes.[5,6] The values for C(6), C(7), C(8), and C(14) are attributed by comparison with those of ergosta-4,6,8-(14),22-tetraene (12c). Again, in that case, we notice the deshielding of the C(18) protons in agreement with the existence of a double bond in ring C.

The fraction of the steroid which had not reacted was carefully analysed by chromatography and shown to contain 31% of coprosta-6,8(14),22-trien-3β-ol (*cis* A/B junction), a compound isolated previously by us [10] during the $RhCl_3$-catalysed isomerisation of ergosterol. The remaining more polar steroid portion was a mixture of ergosterols B_1 and B_2.

We have shown during a former study [10] that only equimolecular amounts of HCl were required for the protonation of ergosterol at C(5) and that this low concentration of acid was limiting the process of double-bond migration. Thus it is obvious that small quantities of HCl which are formed during the palladisation process react readily with the starting material to give (10) and ergosterol B_2. The latter may then be rearranged under the influence of the organometallic species to afford ergosterol B_1. Removal of HCl by addition of sodium carbonate to the reaction mixture produced, in low yield, a complex which was difficult to purify and we noticed that the steroid which had not reacted consisted largely of unaltered ergosterol.

The complexes (9) do not show the complicated stereochemistry encountered with complexes of vitamin D and of various cholestenes.[9] The ^{13}C n.m.r. spectra showed only a single resonance for each carbon atom. It was not possible to identify precisely the C(19) protons among the other methyl group signals although their resonance was not in the δ 1.5 region where absorption of the methyl group in a β-(3—5η) complex has been observed.[9] On the basis of other structural assignments [11] and on the results described later we can attribute the α-configuration to the complexes (9).

Complex (9a) was also obtained in almost quantitative yield after a few minutes in the reaction of 3-*epi*-ergosterol (8c) [1] with (1). If departure of the leaving group is assisted by a *trans*-participation of the metal, preferential β-complexation should be observed. This is not

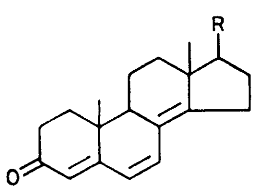


SCHEME

seen and the hydroxy-group must play another role. Convincing experiments with labelled steroids [12] have shown that formation of cholest-4-ene–palladium complexes starts by co-ordination of the double bond and is followed by hydrogen abstraction on the side of complexation. Thus, it seems reasonable to propose that hydrogen is removed as H^+ and that an eliminating ligand acts as proton acceptor. For steric reasons already noted in these series [1] complexation at the α-side is much preferred. The following step most probably involves protonation of the OH group which is much easier when it is located on the same side as in the 3-*epi*-ergosterol case (8c). Departure of water (Scheme) may then be assisted by elimination of 14-H and by rearrangement of the double bonds, the driving force for this reaction being the formation of a thermodynamically more stable endocyclic complex.

Two synthetically useful reactions have been performed with complexes (3) and (9), which offer additional arguments in favour of their structures. Reduction of the complexes can be effected instantaneously by all the classical reducing agents. To avoid further hydrogenation by very reactive metal hydrides generated *in situ* we have found it preferable to use the monohydride $HLiAl(OBu^t)_3$. Thus complexes (3a) or (9a) are respectively converted into the known isotachysterol-2 (11) [13] and the tetraene (12c).[14]

Transition-metal complexes may be expected to react with hydroperoxides by electron transfer or by co-ordination followed by oxygen transfer to oxidisable ligands.[15] In the latter case, production of allylic alcohols has been shown to occur both regio- and stereo-selectivity.[16] Oxidation of complex (9a) by *m*-chloroperoxybenzoic acid afforded in good yield the alcohol (12a) whose structure was confirmed by formation of the epimer (12b) after reduction of the tetraenone



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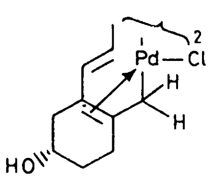

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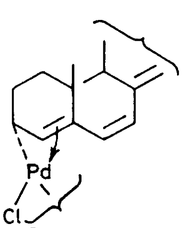

(15)

(13).[17] Less good results were obtained by oxidation of complexes (3) which was shown to occur with very little regio- and stereo-selectivity.

These synthetic manipulations prove structures (3) and (9) and the α-stereochemistry of complexes (9). For the two complexes, the limiting structures (14) and (15), with a high degree of double-bond character for the metal-bonded carbon atoms **19** or **3**, must be considered. They account for the chemical reactivity of these complexes.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus and are uncorrected. I.r. spectra were recorded for Nujol mulls with a Unicam SP 1100 spectrophotometer. N.m.r. spectra were taken for solutions in $CDCl_3$ (Me_4Si as internal standard) with a Varian A-60 spectrometer for ^1H and a Brucker WP 80 spectrometer for ^{13}C. The ^{13}C spectra were recorded with total decoupling, off-resonance, and with the low-noise technique to localise the tetrasubstituted carbon atoms. Optical rotations were determined for solutions in $CHCl_3$ on a Perkin-Elmer 241 MC Polarimeter. Both thin-layer and plate chromatography were carried out on Merck Keiselgel plates. Light petroleum refers to the fraction of b.p. 40—60 °C and the solvent mixtures are described in ratios of volume. Osmometric determinations were obtained for $CHCl_3$ solutions by the Analytical Laboratory, Imperial College (London). Anhydrous magnesium sulphate was used for drying solutions. All the reactions described were carried out under a nitrogen atmosphere.

Bis[calciferol(chloro)palladium] (3a) *and Bis[cholecalciferol(chloro)palladium]* (3b).—To vitamin D_2 (2a) (1 g, 2.5 mmol) in dry acetone (40 ml) or in chloroform (30 ml) was added in one portion $(PhCN)_2PdCl_2$ (1) (1 g, 2.6 mmol). The mixture quickly became dark red in colour and after 1 h (t.l.c. control) the solution was filtered and concentrated *in vacuo* to 5 ml. Plate chromatography with elution using ether–light petroleum (9 : 1) gave a large yellow strip which was recovered and extracted with ether. Evaporation gave complex (3a) as a yellow solid (1.15 g, 85%) which was crystallised from acetone (0.92 g). The same procedure with vitamin D_3 (2b) afforded 0.97 g of pure complex. *Complex* (3a) had m.p. 170—172 °C; $[\alpha]_D$ +186° (*c* 0.156); *M* (osmometry): found 1104 (calc. 1076) (Found: C, 62.2; H, 8.0; Cl, 6.6. $C_{56}H_{86}Cl_2O_2Pd_2$ requires C, 62.7; H, 8.1; Cl, 6.6%). *Complex* (3b) had m.p. 174°; $[\alpha]_D^{22}$ +167° (*c* 0.123); *M*: found 1 089 (calc. 1 050) (Found: C, 61.3; H, 8.3; Cl, 6.9. $C_{54}H_{86}Cl_2O_2Pd_2$ requires C, 61.8; H, 8.2; Cl, 6.9%).

Calciferol(chloro)triphenylphosphinepalladium Complex (6a).—To complex (3a) (0.5 g, 0.5 mmol) in dichloromethane was added triphenylphosphine (0.269 g, 1 mmol). After a few minutes the solvent was removed and the monomer purified by chromatography (elution with ether) and crystallisation (acetone) to afford 0.65 g of the pure *monomeric complex* (6a) (yellow crystals), m.p. 155—157 °C (Found: C, 68.9; H, 7.3. $C_{46}H_{58}ClOPPd$ requires C, 69.1; H, 7.3%).

Complex (6b).—*Complex* (6b) was obtained as just described, from (3b), m.p. 96—97 °C (Found: C, 68.5; H, 7.6. $C_{45}H_{58}ClOPPd$ requires C, 68.6; H, 7.4%).

Complexation of Ergosterol (8a) *and of* 7,8-*Didehydrocholesterol* (8b).—To a solution of ergosterol (8a) (2 g) in chloroform (50 ml) was added at room temperature a slight excess (2.2 g) of compound (1). After 2 h the volume was reduced *in vacuo* to 8 ml and the mixture was chromatographed on silica plates with light petroleum–ether (8 : 3) as eluant. The yellow-brown strip was extracted with ether to afford, after removal of the solvent, complex (9a) as a brown solid (1.6 g, 62%) which was crystallised from ether at −20 °C. The more polar fraction was recovered by extraction with ether and gave a white residue (0.52 g) after removal of the solvent. Several portions of this residue were combined and chromatographed on fluorescent silica plates (ether–light petroleum, 1 : 2) to afford 0.38 g of compound (10) (R_F 0.3) and 1.22 g of a mixture of ergosterols B_1 and B_2 (R_F 0.2) which was shown by n.m.r. spectroscopy to contain *ca.* 15% of the latter.

The same procedure was applied to (8b) (2 g) to give the pure complex (9b). *Bis[chloro(ergosterol)palladium]* (9a) had m.p. 153—155 °C; $[\alpha]_D^{22}$ +2 170° (*c* 0.159); *M* (osmometry): found 1 066, (calc. 1 038) (Found: C, 64.4; H, 8.1; Cl, 6.5. $C_{56}H_{82}Cl_2Pd_2$ requires C, 64.7; H, 7.9; Cl, 6.8%). *Bis[chloro(7,8-didehydrocholesterol)palladium]* (9b) had m.p. 154—156 °C; $[\alpha]_D$ +2 220° (*c* 0.154), *M*: found 1 091 (calc. 1 014) (Found: C, 64.2; H, 8.0; Cl, 6.6. $C_{54}H_{82}Cl_2Pd_2$ requires C, 63.9; H, 8.1; Cl, 7.0%). Compound (10) had m.p. 87—88 °C (from methanol); $[\alpha]_D^{22}$ +77° (*c* 0.66) {lit.,[10] m.p. 88 °C; $[\alpha]_D$ +75° (*c* 0.81)}; δ 4.08 (3-H, $W_{\frac{1}{2}}$ 7 Hz), 5.18—5.27 (22- and 23-H), 5.5 (6-H, d of d, $J_{6,7}$ 10 Hz, $J_{5,6}$ 5.4 Hz), and 6.09 (7-H, $J_{6,7}$ 10 Hz).

Complexation of 3-epi-*Ergosterol* (8c).—To 3-*epi*-ergosterol (8c) (0.5 g) in chloroform (10 ml) was added (1) (0.6 g). After 2 min all the steroid had reacted (t.l.c.). Treatment as described for ergosterol afforded crude material (0.6 g) which after crystallisation gave complex (9a) (0.54 g, 83%), m.p. 153—154 °C, mixed m.p. with (9a) prepared as already described not depressed, $[\alpha]_D$ +2 194° (*c* 0.153).

Reduction of Complexes (3a) *and* (9a).—To a solution of the complex (0.3 g) in anhydrous ether (50 ml) was added in several portions $HLiAl(OBu^t)_3$ (1 g). After 1 h at room temperature the mixture was black. Water (50 ml) was added. The organic layer was decanted off, washed with brine, and dried, and the solvent removed, to give the crude products (11) and (12c) quantitatively. The crude compounds were purified by literature procedures, and the physical and spectroscopic characteristics of the pure products (11) and (12c) were in agreement with the literature.[13,14]

Synthesis of the Tetraenone (13) *and Ergosta*-4,6,8(14),22-*tetraen*-3β-*ol* (12b).—The ketone (13) [17] was obtained in 65% yield by reaction of ergosta-4,7,22-trien-3-one (0.5 g; from chromate oxidation of ergosterol) in chloroform (10 ml) with compound (1) (0.5 g) for 24 h at room temperature or 3 h at reflux. The reaction was not catalytic and the ketone (13) was formed by decomposition of an unstable complex detected by t.l.c. Alternatively, the ketone (13) was also obtained by reaction of ergosta-4,7-22-trien-3-one with dichlorodicyanobenzoquinone.[18]

A solution of (13) (0.3 g) in dry ether (20 ml) was added at 0 °C to a mixture of $LiAlH_4$ (0.2 g) and dry ether (10 ml). After 30 min, water was added and conventional work-up afforded a quantitative yield of the *alcohol* (12b) which was purified by p.l.c. When crystallised from acetone and dried *in vacuo*, this had m.p. 119—121 °C, $[\alpha]_D$ +178° (*c* 1.38), δ 4.33 (3-H, $W_{\frac{1}{2}}$ 20 Hz), 5.15—5.24 (22- and 23-H), 5.43 (4-H), and 5.86 and 6.21 (each d, *J* 10 Hz, 6- and 7-H) (Found: C, 85.4; H, 10.8. $C_{28}H_{42}O$ requires C, 85.2; H, 10.7%).

Oxidation of Complex (9a).—To a stirred solution of (9a) (0.5 g) in ether–light petroleum (1 : 1; 120 ml) was added *m*-chloroperoxybenzoic acid (0.3 g). After 10 min (t.l.c. control) the mixture was filtered, washed with sodium carbonate solution, then with water, and dried. After removal of the solvent and p.l.c. white crystals of the *alcohol* (12a) (0.29 g) were obtained. When crystallised from acetone this had m.p. 125—127 °C, $[\alpha]_D$ +458° (*c* 0.47), $\lambda_{max.}$ 285 nm (ε 29 000), δ 4.15 (3-H, $W_{\frac{1}{2}}$ 10 Hz), 5.15—5.22 (22- and 23-H), 5.50 (4-H, d, *J* 5 Hz), and 5.77 and 6.17 (each d, *J* 10 Hz, 6- and 7-H) (Found: C, 85.3; H, 10.9. $C_{28}H_{42}O$ requires C, 85.2; H, 10.7%).

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