Studies in the Steroid Group. Part LXX. Reactions at $C_{(11)}$ in 9β-Steroids.*

By A. CRAWSHAW, H. B. HENBEST, E. R. H. JONES, and A. A. WAGLAND.

[Reprint Order No. 6414.]

The 11α-alcohol is the only epimer produced by the reduction under various conditions of an 11-ketone with an adjacent 9β-configuration. In hydrogenation and lithium aluminium hydride reduction the reactions provide further examples of the greater accessibility of the β-face of 9β-steroids (earlier examples, *J.*, 1953, 2921; *J.*, 1954, 728). Δ^{11}-Compounds are described in the 9α- and the 9β-series; in the latter, hydrogenation affords a saturated 9β-stanol (9β-ergostan-3β-ol). The possible conformations of 9β-steroids are discussed.

THE boron trifluoride-catalysed isomerisation of Δ^7-9α : 11α-epoxides of the steroid series to Δ^7-11-ketones [*e.g.*, (I)] with an " unnatural " 9β-configuration has been described in detail (Bladon, Henbest, Jones, Lovell, Wood, and Woods; Elks, Evans, Hathway, Oughton, and Thomas, *J.*, 1953, 2921; cf. also Heusler and Wettstein, *Helv. Chim. Acta*, 1953, **36**, 398). In contrast to Δ^7-steroids with a 9α-configuration, Δ^7-bonds in 9β-compounds were found to be readily hydrogenated, 7 : 8β-dihydro-products [*e.g.*, (II)] being formed stereospecifically. Both ketones (I) and (II) could be isomerised to more stable 9α-compounds of the natural series.

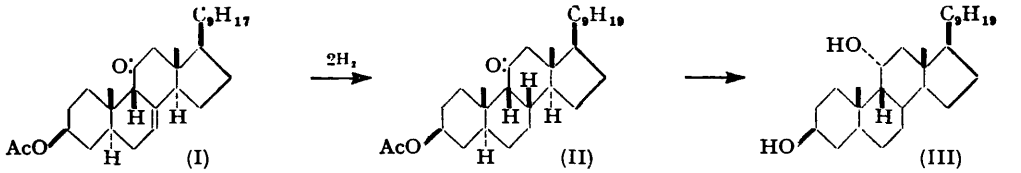
As part of a study of the chemistry of steroid compounds with unusual stereochemical features, reduction of 11-ketones (II) of the 9β-series has been investigated. With lithium aluminium hydride or lithium–ammonia–ethanol, the ketone (II) gave the *same* 3 : 11-diol in high yield, none of the epimeric 11-alcohol being detected by chromatographic techniques. [Sodium–ethanol reduction was less satisfactory, some epimerisation occurring at $C_{(9)}$ before reduction.] These results may be contrasted with the position in the 9α-series where lithium aluminium hydride gives (axial) 11β-alcohols and metal–alcohol reduction affords (equatorial) 11α-alcohols, both formed in high yields.

Hydrogenation of ketones in acidic solution often affords the less stable isomer (axial in

* Part LXIX, *J.*, 1955, 2477.

*cyclo*hexane series), and attempts were thus made to prepare the epimeric 11-alcohol from the ketone (II). However, in only one experiment was an 11-alcohol isolated, and this proved to be identical with that already encountered; if any of the epimer was produced in this reaction the yield must have been very small. Alkaline epimerisation of the new 11-alcohol was not studied as the reaction would have to proceed *via* the 9β-11-ketone (II) under conditions sufficiently alkaline to cause epimerisation of this intermediate to the 9α-11-ketone.

The new 3 : 11-diol of the 9β-series was converted into a 3β-monoacetate by acetylation at 20°, and into a diacetate by acetylation at 90° (acetic anhydride–pyridine). The reactivity of the 11-hydroxyl group towards acylation is thus intermediate between those of 11α- and 11β-hydroxy-groups in the 9α-series. The 11-hydroxyl group in the new diol



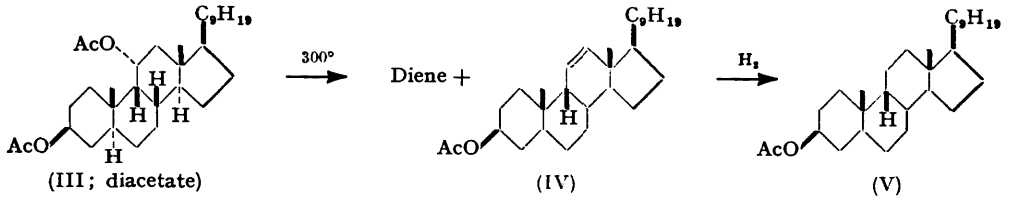
has been assigned an α-configuration (III) on evidence from (*a*) optical rotations and (*b*) olefin formation under various conditions. Klyne and Stokes (*J.*, 1954, 1979) have shown that the optical rotation contributions of hydroxyl (and derived ester) groups in alicyclic compounds containing the grouping $\begin{matrix}C\\C\end{matrix}$>CH·CH(OR)·$CH_2$· may be correlated with the configuration of the alcohol. From our data presented in the Table it can be seen that the negative contribution of the 11-hydroxyl group in our alcohol (III), and the much larger negative contribution of the 11-acetate, correspond to α-configurations.

	$[M]_D$ Values					Δ Values			
	C_{11}-Substituents					α-Substituents		β-Substituents	
Parent compound	H	α-OH	α-OAc	β-OH	β-OAc	ΔOH	ΔOAc	ΔOH	ΔOAc
Ergostanol	+64°	−9°	—	+118°	+208°	−73°	—	+58°	+144°
Ergostanyl acetate ...	+27	—	−105°	+115	+155	—	−132°	+88	+128
9β-Ergostanol	+160	+150	—	—	—	−10	—	—	—
9β-Ergostanyl acetate	+121	+115	−8	—	—	−6	−129	—	—

Dehydration of the 3β-monoacetate of (III) by phosphorus oxychloride and pyridine afforded 3β-acetoxyergost-9-ene, but since the 11-epimer was not available, and since this Δ^9-compound is formed from both the 11α- and the 11β-alcohol in the 9α-series (Crawshaw, Henbest, and Jones, *J.*, 1954, 731), the reaction provides no configurational evidence. Treatment of the 3β-monoacetate with hydrochloric acid in acetic acid also readily afforded the Δ^9-olefin—this observation could be taken as indicating a diaxial arrangement of eliminated groups, as Bernstein, Lenhard, and Williams (*J. Org. Chem.*, 1954, **19**, 41) observed (and we have confirmed in the ergostane series) that axial 11β-alcohols in the 9α-series were dehydrated by this reagent whereas the 11α-hydroxy-compounds were acetylated. On the other hand, an axial configuration appears unlikely in view of the formation of the alcohol by metal–alcohol reduction (but see further discussion below).

Thermal decomposition of esters to olefins and acids is known to proceed with *cis*-elimination in *cyclo*hexane compounds. Pyrolysis of the 3 : 11-diacetate of (III) at 300° gave a mixture of diene, acetoxy-olefin, and starting material, readily separated by chromatography. The acetoxy-olefin fraction consisted mainly of 3β-acetoxy-9β-ergost-11-ene (IV). Comparative experiments in the 9α-series with both the 11α- and the 11β-acetate gave similar yields of diene and acetoxy-olefin fractions. Thus the 3β : 11β-diacetate (VI) yielded the Δ^{11}-compound, and the 3β : 11α-diacetate gave the Δ^9-olefin as the major components of the acetoxy-olefin fractions. The structures of the two Δ^{11}-compounds (IV) and (VII) were established by the strong absorption bands in the infrared spectrum in the 700—800 cm.$^{-1}$ region (Henbest, Meakins, and Wood, *J.*, 1954,

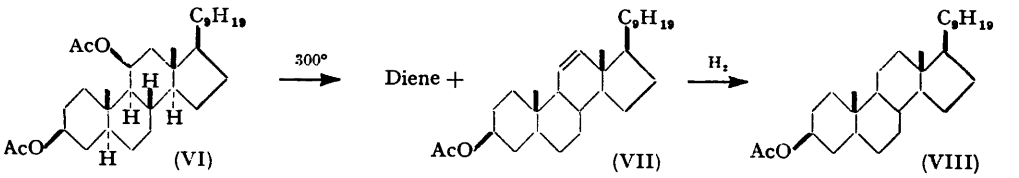
800) and by their further reactions (see below). If $C_{(10)}$ is regarded as an allylic substituent to ring C, the relative rotations of the olefins (IV) and (VII) (latter more positive) fitted the relationship developed for allylic systems by Mills (*J.*, 1952, 4976).



(III; diacetate) (IV) (V)

These results again indicate an 11α-configuration for the hydroxyl group in compound (III) as the formation of Δ^9-olefin as major product is thereby excluded by the *trans*-disposition of the groups to be eliminated.

The possibility that the configuration of the hydroxyl group is 11β, and that *cis*-elimination with 12β-hydrogen is preferred to that with 9β-hydrogen, was also considered. However, the literature indicates that there is a preference for such elimination to occur



(VI) (VII) (VIII)

towards the more substituted position (cf. Barton, *J.*, 1949, 2174; Barton and Rosenfelder, *J.*, 1949, 2459; *J.*, 1951, 1048). Further examples are the preferential formation of $\Delta^{1(9)}$-octalin from *trans*-α-decalol (m. p. 63°) (Hückel and Naab, *Annalen*, 1933, **502**, 136), and the Δ^9-olefin from the 11α-acetate in the 9α-series (above).

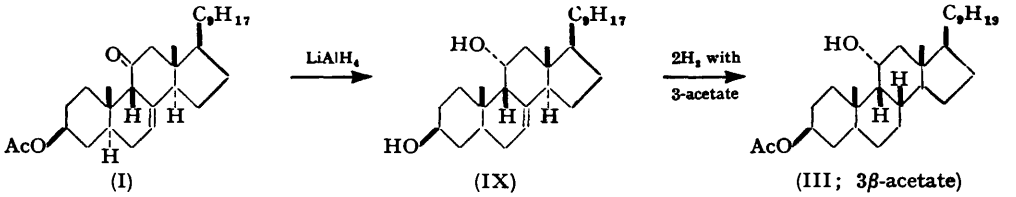
In so far as the relative stabilities of the olefinic products influence the direction of elimination, Δ^9-steroids appear, from the evidence of their invariant formation from 11-oxygenated compounds under " ionic " conditions, to be more stable than Δ^{11}-compounds (cf. Crawshaw, Henbest, and Jones, *loc. cit.*). This may be related in part to the circumstance that Δ^9-bonds lie opposite to the *trans*-ring fusion of rings C and D (cf. stability of Δ^2-compounds in *trans*-A/B series).

Hydrogenation of the Δ^{11}-compounds (IV) and (VII) afforded derivatives of 9β-ergostanol (V) and ergostanol (VIII) respectively. Oxidation of 9β-ergostanol gave the 3-ketone, which readily gave a dinitrophenylhydrazone (11-ketones of the 9β-series do not). The position of the carbonyl stretching frequency in the infrared (1710 cm.$^{-1}$) also indicated the structure of a 3-ketone (the more heavily adjacently alkylated 11-ketones of the 9α- and 9β-series exhibit bands at frequencies just less than 1700 cm.$^{-1}$). These reactions exclude the possibility that the acetoxy-olefin was produced by elimination in ring A; the final ketone would then have been 9β-ergostan-11-one.

Actually the Δ^{11}-compounds were accompanied by smaller amounts of Δ^9-isomers and *vice versa* in these pyrolytic experiments. The proportions of each could be estimated from the intensities of the C–H bending frequencies in the infrared spectrum (see Experimental section). The preferential formation of ring-C rather than ring-A olefins deserves comment, since it might be expected that the former would be more strained, involving flattening of a more rigid part of the molecule. Infrared measurements at room temperature support this suggestion (Henbest, Meakins, and Wood, *loc. cit.*), although of course at the higher temperatures of the elimination reaction the energy relations may be modified. A factor favouring elimination from $C_{(11)}$ could be the greater relief of steric compression in this more crowded part of the molecule.

Reduction of the $\Delta^{7:22}$-11-ketone of the 9β-series (I) by lithium aluminium hydride yielded only the 11α-alcohol (IX), hydrogenated to the saturated alcohol obtained previously. Heusler and Wettstein (*loc. cit.*) have also described this particular reduction.

Upon acetylation of the reaction product they obtained a mono- and a di-acetate which, by analogy with the known relative case of acetylation in the 9α-*series*, were designated as 3β-acetoxy-11β-hydroxy- and 3β : 11α-diacetoxy-compounds respectively. Repetition and further examination of the acetylation has shown that the monacetate is actually the 3-acetate of the 3β : 11α-diol (IX), and the diacetate is the corresponding diester. As in



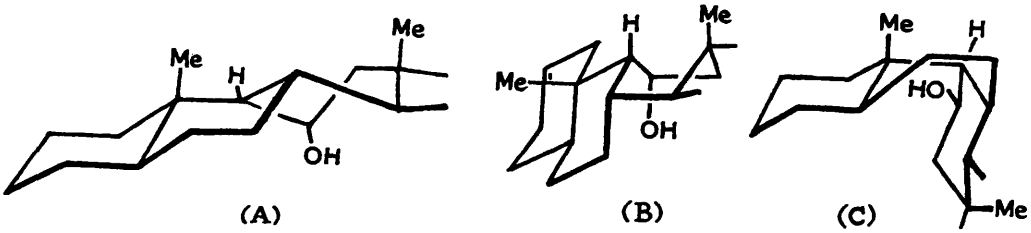
(I) (IX) (III; 3β-acetate)

the 9β-saturated series, the 11α-hydroxy-group in these Δ^7-compounds is acetylated only slowly at 20°, but rapidly at 100°. Dehydration of the 3β-monoacetate of (IX) by phosphorus oxychloride–pyridine afforded the 7 : 9-diene; this was also formed by similar dehydration of the 11β-alcohol produced by reduction of the Δ^7-11-ketone of the 9α-series by lithium aluminium hydride.

Conformation of 9β-*Steroids.*—Inspection of models of a saturated 9β-steroid shows that either ring B or ring C must assume a boat conformation (another form in which B and C are both boat will not be considered). Three models can be constructed (see Figure) and these are readily interconvertible by suitable concerted twisting of bonds (as with the boat forms of *cyclo*hexane and with the two equivalent forms of *cis*-decalin). Conformational analysis of the three structures (Barton, *Experientia*, 1950, **6**, 316; Johnson, *J. Amer. Chem. Soc.*, 1953, **75**, 1498) in an attempt to predict the form of greatest stability showed that no appreciable energy differences would be expected. Thus it seems unlikely that any one rigid conformation would predominate during reactions in solution, but rather that the molecule would adopt the conformation which would give the best transition state or complex for the particular reaction.

Reduction of the 11-ketone by approach of lithium aluminium hydride or hydrogenation catalyst to the β-face of the molecule may involve conformation C, where the angular methyl groups normally hindering β-approach are spread far apart, and ring A shields the 11-ketone from α-approach. In this conformation, the resulting 11α-hydroxyl

Conformations of 9β-*ergostane compounds.*



(A) (B) (C)

A *and* B : 11α-*hydroxyl is boat-axial.* C : 11α-*hydroxyl is equatorial.*

group is also equatorial, in accord with its formation by metal–alcohol reduction. If interconversion of the three conformations is assumed, the ready acid-catalysed dehydration of the 11α-hydroxyl function described above may take place by a normal diaxial elimination from conformation A or B.

Experimental

General experimental directions are as given in Part LXI, *J.*, 1953, 2916.

Reduction of 3β-*Acetoxy*-9β-*ergostan*-11-*one* (II).—(a) *Lithium aluminium hydride.* A solution of the ketone (1 g.) in dry ether (250 c.c.) was heated under reflux for 1 hr. with the

hydride (250 mg.). The product isolated in the usual way was crystallised from methanol, to give 9β-*ergostane*-3β : 11α-*diol* as needles, m. p. 201—205°, $[\alpha]_D$ +45° (Found: C, 80·35; H, 12·1. $C_{28}H_{50}O_2$ requires C, 80·35; H, 12·05%). Acetic anhydride and pyridine at 20° overnight converted the diol in high yield into 3β-*acetoxy*-9β-*ergostan*-11α-*ol* (needles from nitromethane), m. p. 143·5—144·5°, $[\alpha]_D$ +25° (Found: C, 78·15; H, 11·3. $C_{30}H_{52}O_3$ requires C, 78·3; H, 11·4%). Similar acetylation at 100° for 6 hr. afforded 3β : 11α-*diacetoxy*-9β-*ergostane* (needles from aqueous methanol), m. p. 94—95°, $[\alpha]_D$ −1·5° (Found: C, 76·25; H, 10·95. $C_{32}H_{54}O_4$ requires C, 76·4; H, 10·85%).

(b) *Lithium and methanol in liquid ammonia.* Solutions of the 11-ketone (500 mg.) in ether (20 c.c.) and methanol (6 c.c.) in liquid ammonia (150 c.c.) were mixed. Lithium (500 mg.) was added during 15 min. to the stirred solution, followed by ammonium chloride (1 g.) 15 min. later. Isolation with ether, acetylation of the product at 20°, and chromatography on deactivated alumina afforded 3β-acetoxy-9β-ergostan-11α-ol (400 mg.), m. p. and mixed m. p. 138—141°. Alternatively, the reduction product was hydrolysed and chromatographed on alumina (100 g.). The product was homogeneous, all being eluted with benzene–ether (4 : 1) to give the 3β : 11α-diol (450 mg.), m. p. and mixed m. p. 206—207°.

(c) *Hydrogenation in acetic acid.* The ketone (1·5 g.) in acetic acid (400 c.c.) was stirred with Adams catalyst (500 mg.) at 50° in an autoclave containing hydrogen (75 atm.) for 4 hr. The product was chromatographed on alumina (150 g.). Elution with light petroleum–benzene (1 : 1) (1·5 l.) gave starting material (1·2 g.), which crystallised from acetone, then having m. p. 155—156°. Elution with ether–methanol (100 : 1) afforded a gum (300 mg.), which on crystallisation from methanol gave 3β-acetoxy-9β-ergostan-11α-ol, m. p. and mixed m. p. 140—143°, $[\alpha]_D$ +29°. Attempted hydrogenation at atmospheric pressure only gave starting material.

(d) *Hydrogenation in acetic acid and hydrochloric acid.* A solution of the 11-ketone (500 mg.) in acetic acid (50 c.c.) containing hydrochloric acid (2 drops) was shaken in hydrogen until gas absorption ceased (30 min.). Chromatography of the product afforded 3β-acetoxyergostane (270 mg.), m. p. 143—147°, $[\alpha]_D$ +9°, and starting material (220 mg.), m. p. 155—156°.

Dehydration of 3β-*Acetoxyergostan*-11β-*ol.*—The steroid (150 mg.) in acetic acid (10 c.c.) and concentrated hydrochloric acid (1 c.c.) was heated under reflux for 30 min. Isolation with ether and crystallisation from methanol afforded a good yield of 3β-acetoxyergost-9-ene, m. p. 129—130°, $[\alpha]_D$ +15°.

Similar treatment of ergostane-3β : 11α-diol afforded 3β : 11α-diacetoxyergostane, m. p. and mixed m. p. 114—117°.

Dehydration of 3β-*Acetoxy*-9β-*ergostan*-11α-*ol.*—(*a*) A solution of the steroid (280 mg.) in acetic acid (20 c.c.) and concentrated hydrochloric acid (2 c.c.) was heated under reflux for 30 min. Crystallisation of the product from methanol gave 3β-acetoxyergost-9-ene (200 mg.) as fine needles, m. p. and mixed m. p. 126—129°, $[\alpha]_D$ +15°.

(*b*) Phosphorus oxychloride (0·75 c.c.) was added to a solution of the steroid (150 mg.) in pyridine (4 c.c.). After 12 hr., the steroid was isolated with ether. Crystallisation from methanol afforded 3β-acetoxyergost-9-ene (100 mg.), m. p. 131—132°, $[\alpha]_D$ +18°.

Pyrolysis of 3β : 11β-*Diacetoxyergostane.*—The diacetate (500 mg.) was heated at 280—300° for 2 hr. at 200 mm. in a glass retort. The product was chromatographed on alumina (50 g.). Light petroleum (250 c.c.) eluted the diene mixture (40 mg.), which crystallised from methanol as plates, m. p. 84—91° (Found: C, 87·85; H, 11·85. Calc. for $C_{28}H_{46}$: C, 87·7; H, 12·1%). Infrared spectrum: acetate absent. Elution with light petroleum–benzene (1 : 1; 500 c.c.) gave solid (150 mg.), which on crystallisation from acetone afforded 3β-*acetoxyergost*-11-*ene* (VII) as needles, m. p. 129—132°, $[\alpha]_D$ +25° (Found: C, 81·55; H, 11·3. $C_{30}H_{50}O_2$ requires C, 81·4; H, 11·4%). Finally, elution with benzene (250 c.c.) gave starting material (205 mg.). Hydrogenation of 3β-acetoxyergost-11-ene in acetic acid (Adams catalyst) afforded 3β-acetoxyergostane, m. p. and mixed m. p. 146—147°, $[\alpha]_D$ +6°.

The following compounds were also prepared during this study. Lithium aluminium hydride reduction of 3β-acetoxyergostan-11-one gave *ergostane*-3β : 11β-*diol* (plates from acetone), m. p. 175—176°, $[\alpha]_D$ +28° (Found, on sublimed sample: C, 80·2; H, 12·0. $C_{28}H_{50}O_2$ requires C, 80·35; H, 12·05%). Hydrolysis of 3β : 11β-diacetoxyergostane with potassium hydroxide in ethanol at 20° yielded 11β-*acetoxyergostan*-3β-*ol* (fine needles from methanol), m. p. 140—141°, $[\alpha]_D$ +46° (Found: C, 78·3; H, 11·45. $C_{30}H_{52}O_3$ requires C, 78·2; H, 11·4%). Oxidation of this compound with chromic acid in acetone (cf. *J.*, 1951, 2402) afforded 11β-*acetoxyergostan*-3-*one* (needles from acetone), m. p. 136—138°, $[\alpha]_D$ +50° (Found: C, 78·55; H, 11·2. $C_{30}H_{50}O_3$ requires C, 78·55; H, 11·0%).

Pyrolysis of 3β : 11α-*Diacetoxyergostane.*—The diacetate was pyrolysed as described above.

Chromatography gave diene (30 mg.), a mixture of acetoxy-olefins (130 mg.), and starting material (250 mg.). The acetoxy-olefin fraction had m. p. 120—122°; it contained 70% of the Δ^9-compound (see below for infrared data) but this could not be obtained pure by crystallisation, owing to the smaller solubility of the Δ^{11}-isomer.

Pyrolysis of 3β : 11α-*Diacetoxy*-9β-*ergostane*.—Pyrolysis as above gave diene (30 mg.), acetoxy-olefin fraction (210 mg.), and starting material. Crystallisation of the olefin fraction from methanol yielded 3β-*acetoxy*-9β-*ergost*-11-*ene* (IV) as plates, m. p. 114—116°, $[\alpha]_D$ −65° (Found : C, 81·5; H, 11·45. $C_{30}H_{50}O_2$ requires C, 81·4; H, 11·4%). Hydrogenation of the olefin in acetic acid (Adams catalyst) afforded 3β-*acetoxy*-9β-*ergostane* (V) (plates from methanol), m. p. 145—148°, $[\alpha]_D$ +48° (Found : C, 81·2; H, 11·8. $C_{30}H_{52}O_2$ requires C, 81·0; H, 11·8%). Alkaline hydrolysis gave 9β-*ergostan*-3β-*ol* (plates from acetone), m. p. 147—148°, $[\alpha]_D$ +40° (Found : C, 83·25; H, 12·7. $C_{28}H_{50}O$ requires C, 83·5; H, 12·5%). Oxidation with chromic acid in acetone yielded 9β-*ergostan*-3-*one* (plates from acetone–methanol), m. p. 150—151°, $[\alpha]_D$ +65° (Found : C, 83·9; H, 11·95. $C_{28}H_{48}O$ requires C, 83·95; H, 12·1%). This ketone gave a 2 : 4-*dinitrophenylhydrazone* (needles from ethyl acetate–methanol), m. p. 223—226° (Found : C, 70·25; H, 9·3; N, 9·6. $C_{34}H_{52}O_4N_4$ requires C, 70·3; H, 9·0; N, 9·65%).

Analysis of the Acetoxy-olefin Fractions from the Pyrolyses.—Olefinic C–H out-of-plane bending frequencies were determined in CS_2 solution with a sodium chloride prism as follows : 3β-acetoxyergost-11-ene, 755 and 722 cm.$^{-1}$; 3β-acetoxy-9β-ergost-11-ene, 764 and 725 cm.$^{-1}$; and 3β-acetoxyergost-9-ene, 824 cm.$^{-1}$. With the Δ^{11}-compounds, the bands at 722 and 725 cm.$^{-1}$ respectively were used as reference bands for analysis of the pyrolysis mixtures. The ε values were computed as before (*J.*, 1954, 800).

	Peak frequency	ε	Δ^9 (%)	Δ^{11} (%)
3β-Acetoxyergost-11-ene	722	60	—	100
3β-Acetoxy-9β-ergost-11-ene	725	56	—	100
3β-Acetoxyergost-9-ene	824	66	100	—
Pyrolysis product from 3β : 11α-diacetoxyergostane	722	22	—	35
	824	47	70	—
Pyrolysis product from 3β : 11β-diacetoxyergostane	722	38	—	65
	824	16	25	—
Pyrolysis product from 3β : 11α-diacetoxy-9β-ergostane	725	37	—	65
	824	25	40	—

Preparation and Reactions of 9β-*Ergosta*-7 : 22-*diene*-3β : 11α-*diol* (IX).—Solutions of 3β-acetoxy-9β-ergosta-7 : 22-dien-11-one (3 g.) in dry ether (100 c.c.) and lithium aluminium hydride (15 c.c. of 0·5M-solution) were mixed and heated under reflux for 1 hr. After isolation with ether, the product was acetylated with acetic anhydride (24 c.c.) and pyridine (60 c.c.) at 20° for 22 hr. This product was chromatographed on deactivated alumina (150 g.). Light petroleum (400 c.c.) eluted material, m. p. 167—173°; further washing with the same solvent (1250 c.c.) gave an oil (800 mg.) which on crystallisation from methanol afforded 3β : 11α-diacetoxy-9β-ergosta-7 : 22-diene as needles, m. p. 151—153°, $[\alpha]_D$ −139° (Found : C, 76·9; H, 9·9. Calc. for $C_{32}H_{50}O_4$: C, 77·05; H, 10·1%). Heusler and Wettstein (*loc. cit.*) give m. p. 145·5—147°, $[\alpha]_D$ −158°, for this compound. Further elution with benzene–ether (9 : 1) afforded 3β-*acetoxy*-9β-*ergosta*-7 : 22-*dien*-11α-*ol* (1·6 g.) (needles from methanol), m. p. 169—173°, $[\alpha]_D$ −114° (Found : C, 79·0; H, 10·55. $C_{30}H_{48}O_3$ requires C, 78·9; H, 10·6%). Heusler and Wettstein give m. p. 166—169°, $[\alpha]_D$ −111°, for this compound which they suggested was 3β-acetoxy-9β-ergosta-7 : 22-dien-11β-ol. Acetylation of 3β-acetoxy-9β-ergosta-7 : 22-dien-11α-ol with acetic anhydride and pyridine at 100° for 6 hr. gave the above diacetate, m. p. 147—150°, $[\alpha]_D$ −140°.

Hydrogenation of 3β-acetoxy-9β-ergosta-7 : 22-dien-11α-ol in acetic acid (Adams catalyst) afforded 3β-acetoxy-9β-ergostan-11α-ol, m. p. 139—142°, $[\alpha]_D$ +23°.

Dehydration of 3β-acetoxy-9β-ergosta-7 : 22-dien-11α-ol with phosphorus oxychloride in pyridine at 20° for 12 hr. gave 3β-acetoxyergosta-7 : 9 : 22-triene, m. p. and mixed m. p. 172—175°, $[\alpha]_D$ +35°.

Preparation and Dehydration of 3β-*Acetoxyergosta*-7 : 22-*dien*-11β-*ol*.—Solutions of 3β-acetoxyergosta-7 : 22-dien-11-one (320 mg.) in ether–dioxan (5 : 1) (6 c.c.) and lithium aluminium hydride (0·45M) (2·5 c.c.) were mixed and then heated under reflux for 1 hr. The steroid was isolated in the usual way, and then acetylated at 20° overnight. Crystallisation from methanol–nitromethane (1 : 1) afforded 3β-*acetoxyergosta*-7 : 22-*dien*-11β-*ol* (210 mg.), m. p. 168—172°, $[\alpha]_D$ −21° (Found : C, 78·8; H, 10·3. $C_{30}H_{48}O_3$ requires C, 78·85; H, 10·6%). Dehydration of this compound (100 mg.) with phosphorus oxychloride (0·5 c.c.) in pyridine (3 c.c.) at 20°

gave a high yield of 3β-acetoxyergosta-7 : 9 : 22-triene, m. p. and mixed m. p. 172—175°, $[\alpha]_D$ +34°.

The authors thank Glaxo Laboratories Ltd. for gifts of chemicals and for financial assistance (to A. C.). One of the authors (A. A. W.) thanks the Department of Scientific and Industrial Research for a Maintenance Grant. Infrared spectra were determined under the direction of Dr. G. D. Meakins, and microanalyses were performed by Messrs. E. S. Morton and H. Swift.

THE UNIVERSITY, MANCHESTER, 13. [*Received, May 11th*, 1955.]