379. *Aspects of Stereochemistry. Part IV.* The Steric Requirement for Hydrogen–Catalyst Induced Migration of the Olefinic Bond.*

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For the isomerisation of an olefinic bond under hydrogenation conditions a *cis*-relation should exist between the entering and leaving hydrogen atoms, and both must be sterically accessible to the catalyst surface. The phenomenon is discussed with particular reference to some new experiments with 8α- and 14β-steroids. Comment is also made upon the greater stability of 1-alkyl*cyclo*pentenes compared with their exocyclic isomers.

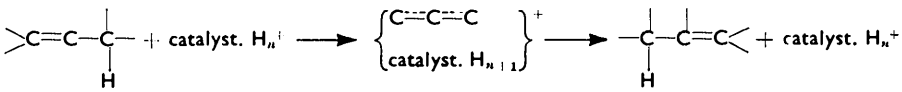
Most olefins can be hydrogenated in the presence of a catalyst to saturated compounds. However, if the olefinic bond is tri- or tetra-alkylated and in a very hindered position (*e.g.* $\Delta^{8(14)}$-steroids, α- and β-amyrins) addition may be impossible under the normal experimental conditions. This paper is concerned with the region between these two extremes, where, for a given olefinic position, either addition or isomerisation to a more stable olefin takes place, the choice of reaction depending on the stereochemical environment of the olefin.

Perhaps the best-known examples [1] of the isomerisation reaction are the conversion of

* Part III, preceding paper.

[1] Fieser and Fieser, "Natural Products Related to Phenanthrene," Reinhold Publ. Corp., New York, 1949, p. 240. Partial steroid formulæ are used throughout this paper in order to emphasize rings B and C.

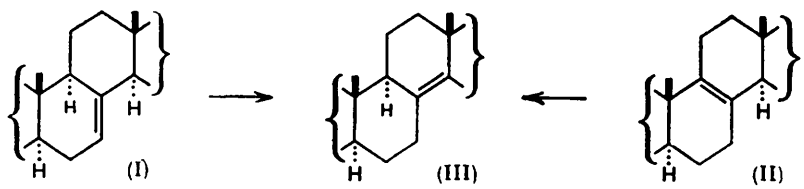
Δ^7- and Δ^8-steroids (I and II, respectively) into $\Delta^{8(14)}$-compounds (III) in the presence of hydrogen and palladium or less effectively platinum. These reactions are more rapid in the presence of weak acids (*e.g.*, acetic acid, not sufficiently strong to cause isomerisation by ordinary solution prototropy), and this fact, together with stereochemical evidence discussed below, leads to the suggestion that a simple picture of the reaction may involve the formation of an allylic carbonium ion–catalyst complex as intermediate stage. An

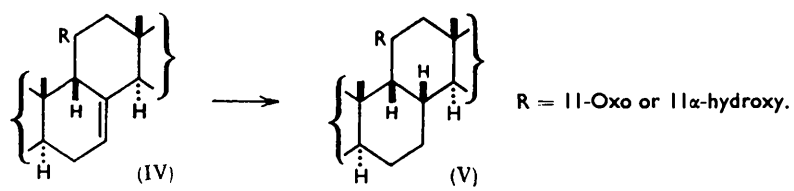


alternative rôle of acid could be initial addition of a proton to give an intermediate " saturated " carbonium ion; the greater general stability of allylic carbonium ions would appear to make them preferable as intermediates.

Isomerisation of a double bond in the presence of hydrogen and catalyst usually takes place with tri- and tetra-substituted olefins.[2] From the examples discussed in this paper it is concluded that for isomerisation to occur (*a*) the allylic hydrogen to be removed must be sterically accessible to the catalyst surface and (*b*) there must be a favourable energy change for the re-entry of hydrogen on the *same* side of the molecule to give an olefin which does not add hydrogen. Thus, with factor (*a*) a reversal of configuration of allylic hydrogen may cause it to become relatively inaccessible to the catalyst, and normal addition of hydrogen may then take place.

In the isomerisation of a Δ^7- or Δ^8-5α-steroid (I or II), the catalyst operates on the rear (α) side of the molecule, well known to be less hindered in compounds with the given stereochemistry. The *cis*-removal and addition of hydrogen on the α-face is easily seen in the conversion of (II) into (III), but complete proof in the conversion of (I) into (III)





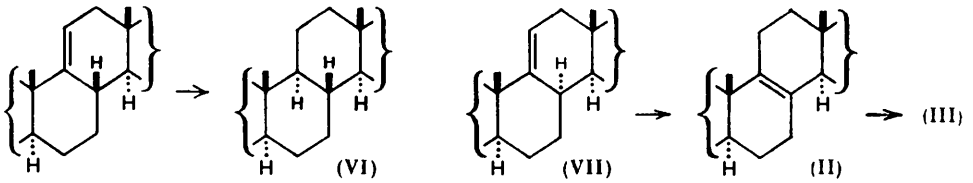
requires the configurational identification of the hydrogen atom added at $C_{(7)}$. It should be possible to test this by using deuterium in place of hydrogen and determining the configuration of the $C_{(7)}$-deuterium (it should be axial 7α) by infrared spectral methods.[3] If the catalyst were not prevented by steric factors from approaching the top (β) face of the Δ^7-compound (I), normal addition at this face would give an all-*trans*–*anti*-molecule with

[2] Howe and McQuillin (*J.*, 1956, 2670) showed that prior isomerisation of 1 : 1-disubstituted olefins to tetrasubstituted olefins takes place in the addition of hydrogen to some 6-*epi*cyperone compounds. Replacement of allylic hydrogen by deuterium occurs in the deuteration of Δ^5-steroids (Fukuchima and Gallagher, *J. Amer. Chem. Soc.*, 1955, **77**, 139). The observations are also explicable in terms of the initial formation of allylic carbonium ion-catalyst complexes.

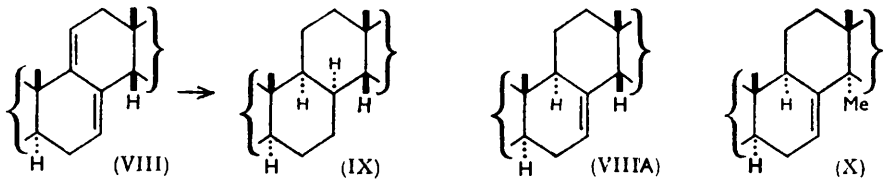
[3] Corey, Howell, Boston, Young, and Sneen, *J. Amer. Chem. Soc.*, 1956, **78**, 5036.

thermochemical stability as great as (probably greater than) that of the $\Delta^{8(14)}$-compound (III) actually formed.

Inversion of the $C_{(9)}$-configuration in the Δ^7-steroid (I) gives a 9β-steroid (IV) in which the steric factors are profoundly altered, for addition of hydrogen [4] now occurs readily at the β-face to yield the saturated system (V). The accessibility of the top face seems to be caused by bending of the molecule, the bulky angular methyl groups being moved farther apart. With β-approach of catalyst, isomerisation to a $\Delta^{8(14)}$-compound is precluded by the α-configuration of the $C_{(14)}$-hydrogen atom.



The rear face of Δ^9-5α-steroids is known to be the less hindered, and hydrogenation proceeds readily to give 9α-compounds (VI). In contrast, attempted hydrogenation of the 8α-isomer (VII; preparation below) has now been found to give a $\Delta^{8(14)}$-olefin (III), obviously *via* the Δ^8-compound (II). Models indicate that the angular methyl groups

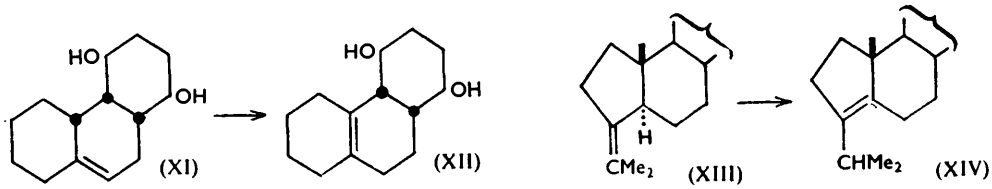


shield the Δ^9-bond from β-approach of reagents, and thus the rearrangement of (VII) to (II) can be envisaged as taking place at the α-face, the hydrogen atom at $C_{(8)}$ having the appropriate α-configuration.

Another example is hydrogenation of the 14β-steroid (VIII) to a saturated compound (IX; see below). There are three possible mono-olefinic intermediates. Initial formation of a Δ^9-compound does not seem likely as the α-approach of catalyst would probably cause isomerisation to the Δ^8-steroid (cf. VII ⟶ II), and this would not be expected to add hydrogen in view of its tetrasubstituted position in the centre of the molecule—although *cis*-addition would give the observed product (IX), the 14β-hydrogen ensuring non-isomerisation to the stable $\Delta^{8(14)}$-olefin. By analogy with the 14α-series, the Δ^7-compound (VIIIA) is the most likely intermediate. Addition of hydrogen at the α-face then gives the saturated compound (IX), the 14β-hydrogen atom again preventing isomerisation to the $\Delta^{8(14)}$-olefin. However, the stereochemistry (8α-hydrogen) of this intermediate and the fact that attempted hydrogenation of the somewhat similar 9α : 14α-dimethyl-Δ^7-compound (butyrospermol; partial formula X) results in migration on the α-face of the double-bond to the Δ^8-position,[5, 6] show that isomerisation of the probable intermediate (VIIIA) to the corresponding Δ^8-steroid (which may or may not add hydrogen) should not be precluded. No final decision can be made at present on whether addition of hydrogen takes place directly to the Δ^7-bond or after its isomerisation to the Δ^8-position, although the former route may be favoured on steric grounds. A tentative explanation of the difference between the Δ^7-compound (VIIIA) which probably adds hydrogen and butyrospermol in which the bond migrates may be provided by the postulate that the addition reaction requires a more intimate olefin–catalyst association than the isomerisation

[4] Bladon, Henbest, Jones, Lovell, Wood, and Woods; Elks, Evans, Hathway, Oughton, and Thomas, *J.*, 1953, 2931.
[5] Dawson, Halsall, Jones, Meakins, and Phillips, *J.*, 1956, 3172.
[6] Lawrie, Hamilton, Spring, and Watson, *J.*, 1956, 3272.

reaction—in the present case the 14α-methyl group in butyrospermol inhibits addition. This suggestion appears reasonable when it is considered that the phenomenon of isomerisation instead of addition is encountered only in somewhat sterically hindered olefins.



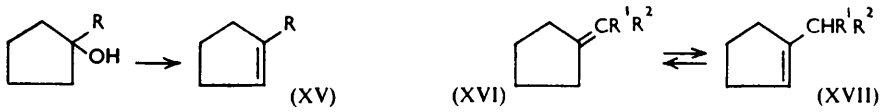
A further example of the isomerisation in which the compounds involved are of established stereochemistry, is the conversion by hydrogen–palladium of the unsaturated diol (XI) into the isomer (XII), observed in the hydrophenanthrene series.[9] The initial molecule (XI) is partly folded in a way favouring approach by catalyst on the same side as the angular hydrogen atoms; the stereochemical requirement for isomerisation is therefore present. Conversion [10] of the *iso*propylidene compound (XIII; anhydro-oleanolic lactone series) into its *cyclo*pentenyl isomer (XIV) in presence of hydrogen and palladium provides another example of the reaction: hydrogen removal takes place from the less-hindered side of the molecule, re-entry of hydrogen not creating a centre of asymmetry in this case.

Included in a generalisation recently made by Brown, Brewster, and Schechter [11] was the statement that " reactions will proceed in such a manner as to favour the formation or retention of an exo double bond in a 5-ring." The isomerisation (XIII) ⟶ (XIV) provides but one example of the many exceptions to this rule; in fact for most five-membered ring systems the rule is more accurately stated as its converse. This is not surprising as there is less eclipsing of the side-chain with ring methylene groups in the endocyclic than in the exocyclic isomer.

Thus only 1-alkyl*cyclo*pentenes (XV) have been identified in the products of dehydration of 1-alkyl*cyclo*pentanols,[12-19] and moreover in the *iso*propyl-*iso*propylidene compounds Wallach and Fleischer [20] isomerised the exocyclic to the endocyclic isomer with dilute acid. None of these simple observations was referred to by Brown, Brewster, and Shechter who mentioned the paucity of examples to support their generalisation for *cyclo*pentane systems. The work of Kon and Linstead and their collaborators referred to by these authors really indicated that in the equilibrium (XVI) ⇌ (XVII) the former was more stable only when very effective conjugation was achieved with R^1 = acetyl or carboxylic ester (R^2 = methyl or hydrogen), for with R^1 = carboxylic acid (? or derived anion) the endocyclic structure (XVII) was favoured at equilibrium. Exocyclic olefins have only been prepared by methods [20-24] (*e.g.*, pyrolysis of suitable βγ-unsaturated acids) precluding

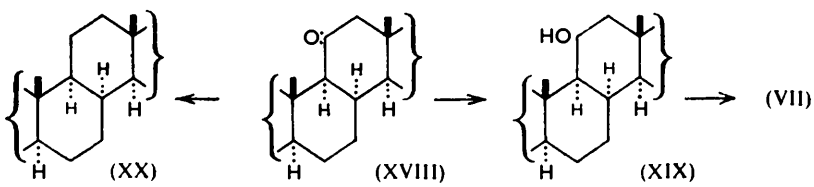
[7] Barton and Cox, *J.*, 1949, 219.
[8] Nes and Mosettig, *J. Org. Chem.*, 1953, **18**, 276.
[9] Robins and Walker, *J.*, 1954, 3960.
[10] Ruzicka, Rudowski, Norymberski, and Jeger, *Helv. Chim. Acta*, 1946, **29**, 210.
[11] Brown, Brewster, and Schechter, *J. Amer. Chem. Soc.*, 1954, **76**, 467.
[12] Chavanne and de Vogel, *Bull. Soc. chim. Belg.*, 1928, **37**, 142.
[13] Skraup and Binder, *Ber.*, 1929, **62**, 1135.
[14] Taft, Levy, Aaron, and Hammett, *J. Amer. Chem. Soc.*, 1952, **74**, 4735.
[15] Bartlett and Barley, *ibid.*, 1938, **60**, 2416.
[16] Meerwein, *Annalen*, 1914, **405**, 156.
[17] Eisenlohr, *Chem. Zentr.*, 1926, **1**, 75.
[18] Zelinskii and Arbuzov, *Chem. Abs.*, 1940, **34**, 2696; Ohta, *ibid.*, 1950, **44**, 9226 (isomerisation of *cyclo*hexene to 1-methyl*cyclo*pentene).
[19] Tatevosyan, Melikyan, and Terzyan, *ibid.*, 1948, **42**, 1570 (dehydration of 1-*cyclo*butylethanol to 1-methyl*cyclo*pentene).
[20] Wallach and Fleischer, *Annalen*, 1907, **353**, 307.
[21] Wallach, *ibid.*, 1906, **347**, 325.
[22] Vogel, *J.*, 1938, 1323.
[23] Arnold, Amidon, and Dodson, *J. Amer. Chem. Soc.*, 1950, **72**, 2871.
[24] van der Bij and Kooyhan, *Rec. Trav. chim.*, 1952, **71**, 837.

the formation of the endocyclic isomer. Evidence for the greater stability of 1-methyl*cyclo*pentene has been given by Turner and Garner.[24a]



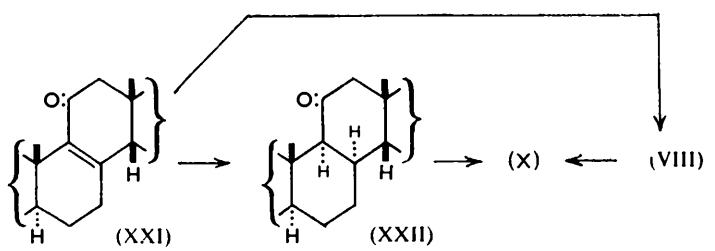
8α-*Steroids*. The 8α-Δ⁹-steroid (VII) was prepared from the 8α-11-ketone [4] (XVIII), 8α-ergostanol series). The preferred conformation of an 8α-steroid has been discussed; [25] ring B is a boat and ring C a chair conformation, the general appearance of the steroid still being approximately flat as in an 8β-compound. It was not surprising therefore that reactions at $C_{(11)}$ of the 8α-compounds resembled closely those of the related 8β-compounds. Thus reduction by lithium aluminium hydride of the 11-ketone afforded the 11β-alcohol (XIX; β-OH) in excellent yield, and reduction with sodium–propanol gave the equatorial 11-alcohol (XIX; α-OH) in high yield. However, acetylation of the 11α-hydroxyl group was more difficult than in the 8β-series, a 3β-monoacetate being isolated from either the 3β : 11α- or 3β : 11β-diol under the usual conditions of room temperature.

Dehydration of either of these monoacetates by phosphorus oxychloride in pyridine gave the Δ⁹-olefin (VII), the yield, as expected, being better from the axial 11β-alcohol.



In the 8β-series both 11-alcohols also give the corresponding Δ⁹-compound.[26] The Δ⁹-compound showed an absorption band at 818 cm.$^{-1}$ characteristic of a trisubstituted olefin.[27] With monoperphthalic acid it afforded an epoxide of probable α-configuration. Wolff–Kishner reduction of the 11-ketone (XVIII), which does not form carbonyl derivatives at room temperature, gave the deoxy-compound (XX).

14β-*Steroids*. In this series the starting material was the conjugated ketone (XXI), conveniently prepared from the isomeric Δ⁷-9β-compound by treatment with alkali.

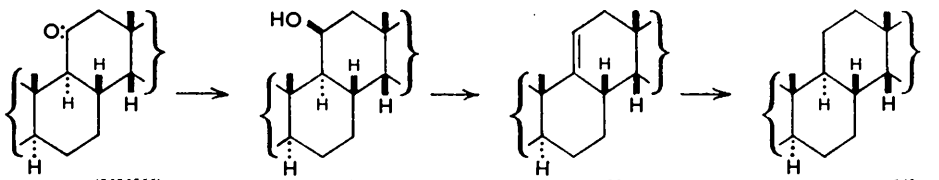


Hydrogenation afforded a saturated ketone, the 8α : 9α-configuration (XXII) of which is suggested by analogy with the steric course of the similar hydrogenation of the 14α-compound,[4] and by conformational arguments.[29] The saturated ketone (XXII), which did not yield a 2 : 4-dinitrophenylhydrazone under normal conditions, was reduced by the Wolff–Kishner method to the deoxy-compound (X). This was identical with the product

[24a] Turner and Garner, *J. Amer. Chem. Soc.*, 1957, **79**, 253.
[25] Clayton, Henbest, and Jones, *J.*, 1953, 2015.
[26] Crawshaw, Henbest, and Jones, *J.*, 1954, 731.
[27] Bladon, Fabian, Henbest, Koch, and Wood, *J.*, 1951, 2402.
[28] Sondheimer, Yashin, Rosenkranz, and Djerassi, *J. Amer. Chem. Soc.*, 1952, **74**, 2696.
[29] Djerassi, Frick, Rosenkranz, and Sondheimer, *ibid.*, 1953, **75**, 3496.

obtained from hydrogenation of the 7 : 9-diene (VIII); the steric course of the hydrogenation was thus established. The 7 : 9-diene (VIII) was obtained by reduction of the conjugated ketone (XXI) with lithium aluminium hydride followed by dehydration of the resulting 11-alcohol with acetic acid. Dehydration with mineral acid gave a mixture of nuclear dienes.

Some further experiments in the 14β-series were directed towards the preparation and reduction of the Δ^9-compound (XXV). Reduction with lithium and ammonia of the conjugated ketone (XXI) gave an 8β : 9α-dihydro-11-ketone (XXIII), the configuration being assigned by analogy with a similar reduction described in the sapogenin series, where the product was degraded to a compound of known stereochemistry.[30] Reduction of the 11-ketone (XXIII) by lithium aluminium hydride, followed by acetylation, afforded a 3-acetoxy-11-alcohol (XXIV). Evidence for an axial β-configuration for the 11-hydroxyl group in (XXIV) was provided by ready dehydration by hydrochloric acid in acetic acid: in the 14α-series where ring C has the same conformation this mixture of acids is known to convert 11α-alcohols into acetates and 11β-alcohols into olefins.[31,32] However, the new olefin was not the Δ^9-compound (XXV), which was prepared by treating the 11-alcohol (XXIV) with phosphorus oxychloride in pyridine. The Δ^9-compound thus obtained showed absorption bands in the infrared region assignable to a trisubstituted bond.[27] Acid converted the Δ^9-compound into the olefin obtained previously, and this was finally assigned a $\Delta^{8(14)}$-structure on the basis of end-absorption measurements.[33] In



(XXIII) (XXIV) (XXV) (XXVI)

this rearrangement catalysed by mineral acid, conformational driving force in the $\Delta^9 \longrightarrow \Delta^8$ stage arises from the greater stability of an olefinic bond in the latter position relative to the *cis*-C/D ring fusion. As the Δ^8-bond still contains a degree of instability from being in an unfavourable position in relation to the *trans*-A/B ring junction, further isomerisation to the more stable $\Delta^{8(14)}$-olefin takes place (cf. the rearrangement of cholest-8-en-3β-ol to its $\Delta^{8(14)}$ isomer catalysed by hydrogen chloride[34]).

The first ($\Delta^9 \longrightarrow \Delta^8$) stage suggests that the latter olefin is the more stable. If the steric situation during hydrogenation allowed β-approach of catalyst to the Δ^9-8β-system isomerisation to the Δ^8-compound should (initially) occur. Actually addition of hydrogen takes place, the reaction being envisaged as proceeding on the α-face to give 14β-ergostanol (XXVI). These reactions in the 14β-series proceed therefore very similarly to those with 14α-steroids, except that there is probably more driving force for the $\Delta^9 \longrightarrow \Delta^8$ rearrangement in the new series.

Experimental

In this and the following paper rotations were determined in chloroform and ultraviolet absorption in ethanol solutions.

3β-*Acetoxy*-8α-*ergostan*-11-*one* (XVIII).—A solution of 3β-acetoxyergosta-8 : 22-dien-11-one (2·5 g.) in ethanol (150 c.c.) was shaken with hydrogen in the presence of palladium–charcoal (4%; 2 g.) until a sample of product showed an ε_{2550} value <300; the uptake of hydrogen was

[30] Djerassi and Thomas, *Chem. and Ind.*, 1954, 1228.
[31] Bernstein, Lenhard, and Williams, *J. Org. Chem.*, 1954, **19**, 41.
[32] Crawshaw, Henbest, Jones, and Wagland, *J.*, 1955, 3420.
[33] Bladon, Henbest, and Wood, *J.*, 1952, 2737.
[34] Wieland and Görnhardt, *Annalen*, 1946, **557**, 248.

then about 2·7 mol. The product was chromatographed on alumina (60 g.). Elution with benzene–light petroleum (100 c.c.; 1 : 4) gave 3β-acetoxyergost-8(14)-ene, m. p. and mixed m. p. 108°. Elution with benzene and crystallisation of the product from methanol gave the 11-ketone (0·51 g.), m. p. 163—164°, $[\alpha]_D$ −10·5°. Alkaline hydrolysis of the acetate gave 3β-*hydroxy*-8α-*ergostan*-11-*one*, m. p. 151—154°, $[\alpha]_D$ −33° (Found: C, 79·0; H, 11·4. $C_{28}H_{48}O_2,\frac{1}{2}H_2O$ requires C, 79·1; H, 11·5%).

8α-*Ergostane*-3β : 11β-*diol* (XIX; β-OH).—The 11-ketone (72 mg.) and lithium aluminium hydride (50 mg.) in ether (20 c.c.) were heated under reflux for 45 min. Crystallisation of the product from acetone yielded the 3β : 11β-*diol* (62 mg.), m. p. 195—198°, $[\alpha]_D$ −14° (Found: C, 80·05; H, 12·0. $C_{28}H_{50}O_2$ requires C, 80·3; H, 12·0%).

Acetylation of this diol with acetic anhydride–pyridine at 20° overnight gave, after crystallisation from aqueous acetone, the 3β-*monoacetate*, m. p. 175—178°, $[\alpha]_D$ +10° (Found: C, 78·25; H, 11·4. $C_{30}H_{52}O_3$ requires C, 78·2; H, 11·4%).

8α-*Ergostane*-3β : 11α-*diol* (XIX; α-OH).—Sodium (2 g.) was added during 30 min. to a boiling solution of 3β-acetoxy-8α-ergostan-11-one (0·2 g.) in propanol (50 c.c.). When the metal had dissolved the propanol was distilled off and the steroid isolated with ether. Crystallisation from aqueous acetone gave the 3β : 11α-*diol* (0·17 g.) as needles, m. p. 203—205°, $[\alpha]_D$ −46° (Found: C, 78·3; H, 11·9. $C_{28}H_{50}O_2,\frac{1}{2}H_2O$ requires C, 78·6; H, 12·0%). Acetylation of the diol as before yielded the 3β-*acetate*, m. p. 187—190°, $[\alpha]_D$ −65° (Found: C, 78·4; H, 11·65. $C_{30}H_{52}O_3$ requires C, 78·2; H, 11·4%).

3β-*Acetoxy*-8α-*ergost*-9-*ene* (VII).—(*a*) Phosphorus oxychloride (0·9 c.c.) was added to 3β-acetoxy-8α-ergostan-11β-ol (0·19 g.) in pyridine (7·5 c.c.) containing a drop of water. Crystallisation of the product from acetone gave 3β-*acetoxy*-8α-*ergost*-9-*ene* (0·11 g.) as needles, m. p. 88—92°, $[\alpha]_D$ +108° (Found: C, 81·1; H, 11·4. $C_{30}H_{50}O_2$ requires C, 81·4; H, 11·4%). Addition of *N*-ethylpiperidine (1 c.c.) to the initial mixture improved the yield from 60 to 85%.

(*b*) Similar dehydration of the 3β-acetoxy-11α-alcohol gave a 35% yield of 3β-acetoxy-8α ergost-9-ene, chromatographic purification being necessary in this case.

Hydrogenation of 3β-*Acetoxy*-8α-*ergost*-9-*ene*.—The steroid (84 mg.) in acetic acid (20 c.c.) was shaken in hydrogen in the presence of Adams's catalyst (75 mg.) for 3 hr.; no hydrogen was absorbed. Crystallisation from aqueous acetone yielded 3β-acetoxyergost-8(14)-ene (79 mg.), m. p. and mixed m. p. 107—109°.

Epoxidation of 3β-*Acetoxy*-8α-*ergost*-9-*ene*.—The olefin (0·6 g.) dissolved in dry ether (50 c.c.) was treated with monoperphthalic acid (2 mol.) in ether, the mixture then being kept at 25° for 2 days. Isolation of the steroid with ether followed by crystallisation from methanol yielded the 9α : 11α-*epoxide*, m. p. 132—134°, $[\alpha]_D$ +18·5° (Found: C, 78·7; H, 11·1. $C_{30}H_{50}O_3$ requires C, 78·55; H, 11·0%).

8α-*Ergostan*-3β-*ol* (XX).—A mixture of 3β-acetoxy-8α-ergostan-11-one (167 mg.), hydrazine hydrate (2 c.c.; 90%), and sodium methoxide in methanol (5 c.c.; 10%) was heated in a sealed tube at 170° for 20 hr. and then at 205° for 24 hr. Crystallisation of the product from aqueous methanol gave 8α-*ergostan*-3β-*ol* (118 mg.) as plates, m. p. 123—126°, $[\alpha]_D$ +43° (Found: C, 83·65; H, 12·55. $C_{28}H_{50}O$ requires C, 83·5; H, 12·5%).

Preparation of 3β-*Hydroxy*-14β-*ergosta*-7 : 9 : 22-*triene* (VIII).—Potassium hydroxide (20 g.) in water (20 c.c.) was added to boiling 3β-acetoxy-11-oxo-9β-ergosta-7 : 22-diene (15 g.) in ethanol (200 c.c.) under nitrogen. The solution was then heated under reflux for 4 hr. under nitrogen, and the steroid isolated with ether. Acetylation followed by crystallisation from methanol afforded 3β-*acetoxy*-11-*oxo*-14β-*ergosta*-8 : 22-*diene* (12·5 g.) as needles, m. p. 110—113°. The pure compound had m. p. 113—115°, $[\alpha]_D$ +117° (Found: C, 79·2; H, 10·15. $C_{30}H_{46}O_3$ requires C, 79·2; H, 10·2%). This compound was also prepared by similar treatment of the corresponding 9α-unconjugated ketone or 14α-conjugated ketone.

Solutions of the ketone (6·64 g.) in dry ether (100 c.c.) and lithium aluminium hydride (2·72 g.) in dry ether (400 c.c.) were mixed and then heated under reflux for 4 hr. The product, isolated with ether, showed no selective absorption in the 2400 Å region. The product was heated in acetic acid (50 c.c.)–acetic anhydride (50 c.c.) for 1 hr. on the steam-bath. Isolation with ether afforded 3β-*acetoxy*-14β-*ergosta*-7 : 9 : 22-*triene* (VIII), m. p. 63—64° (from methanol), $[\alpha]_D$ −30° (Found: C, 82·0; H, 10·85. $C_{30}H_{46}O_2$ requires C, 82·1; H, 10·6%). The corresponding *alcohol* had m. p. 117—120° (from methanol), $[\alpha]_D$ −39° (Found: C, 84·7; H, 11·2. $C_{28}H_{44}O$ requires C, 84·8; H, 11·2%). Ultraviolet absorption: $\lambda_{max.}$ 2400 Å (ε 16,100).

8α : 14β-*Ergostanol* (IX).—(*a*) The foregoing trien-3β-ol (0·1 g.) in acetic acid (6 c.c.) was shaken in hydrogen with Adams's catalyst (0·1 g.) for 1 hr. Filtration and evaporation under reduced pressure and crystallisation from methanol gave 8α : 14β-*ergostanol* as needles, m. p. 98—101°, $[\alpha]_D$ +33° (Found : C, 83·3; H, 12·4. $C_{28}H_{50}O$ requires C, 83·5; H, 12·5%). The ergostanol showed negligible absorption in the 2000—2200 Å region, and gave no colour with tetranitromethane.

(*b*) Sodium (1·9 g.) was dissolved in methanol (20 c.c.), 3β-acetoxy-8α : 14β-ergostan-11-one (0·17 g.) and hydrazine hydrate (90%; 9 c.c.) were added, and the solution was heated at 200° for 48 hr. in a steel autoclave. Several crystallisations of the product from methanol gave 8α : 14β-ergostanol (37 mg.) as needles, m. p. and mixed m. p. 98—101°, $[\alpha]_D$ +32°.

Oxidation of the alcohol by chromic acid–acetone [28] gave 8α : 14β-*ergostanone*, m. p. 97—99° (from methanol), $[\alpha]_D$ +51° (Found : C, 84·2; H, 12·1. $C_{28}H_{48}O$ requires C, 83·9; H, 12·1%). Reduction with sodium borohydride in aqueous dioxan gave back 8α : 14β-ergostanol, m. p. 99—100°.

3β-*Acetoxy*-8α : 14β-*ergostan*-11-*one* (XXII).—3β-Acetoxy-11-oxo-14β-ergosta-8 : 22-diene (2 g.) in ethanol (100 c.c.; freshly distilled from potassium hydroxide) was shaken with hydrogen in the presence of 5% palladised charcoal (1·3 g.). After 16 hr. the reaction was almost complete (light absorption). Chromatographic purification of the product afforded the *ketone* (1·1 g.), m. p. 71—74° (from methanol), $[\alpha]_D$ +60° (Found : C, 78·45; H, 11·25. $C_{30}H_{50}O_3$ requires C, 78·55; H, 11·0%). The infrared spectrum confirmed the presence of acetate and 11-ketone groups. Treatment overnight with boiling ethanolic potash, followed by reacetylation, gave back starting material.

3β-*Acetoxy*-11-*oxo*-14β-*ergost*-22-*ene* (XXIII).—3β-Acetoxy-11-oxo-14β-ergosta-8 : 22-diene (4·4 g.) in dry ether (50 c.c.) was run with stirring into lithium (0·25 g.) in liquid ammonia (250 c.c.). As the blue colour had then disappeared more lithium was added with stirring until it persisted. Ammonium chloride (5 g.) was added and the steroid isolated with ether and then acetylated. Chromatographic purification yielded the 11-*ketone* (2·0 g.) (needles from methanol), m. p. 91—94°, $[\alpha]_D$ +38° (Found : C, 78·6; H, 10·55. $C_{30}H_{46}O_3$ requires C, 78·9; H, 10·6%). The compound showed no high-intensity absorption in the near-ultraviolet region. It was unchanged after vigorous treatment with alkali followed by reacetylation.

3β-*Acetoxy*-14β-*ergosta*-9 : 22-*diene* (XXV).—The foregoing ketone (1 g.) in dry ether was added to lithium aluminium hydride (1 g.) in ether (120 c.c.) and the mixture heated under reflux for 4 hr. The steroid was isolated with ether and acetylated overnight at 20° with acetic anhydride–pyridine, and the product crystallised from methanol, yielding the 11β-*alcohol* (XXIV) (0·39 g.) as needles, m. p. 122—124°, $[\alpha]_D$ +38° (Found : C, 78·8; H, 10·9. $C_{30}H_{50}O_3$ requires C, 78·55; H, 11·0%). The infrared spectrum confirmed the presence of hydroxyl and acetate groups.

Phosphorus oxychloride (1 c.c.; freshly distilled from P_2O_5) was added to the 11-alcohol (0·15 g.) in dry pyridine (10 c.c.), and the mixture kept at 20° overnight. Crystallisation from methanol gave the 9 : 22-*diene* (XXV) as needles, m. p. 61—63°, $[\alpha]_D$ +32° (Found : C, 81·65; H, 10·95. $C_{30}H_{48}O_2$ requires C, 81·8; H, 11·0%).

14β-*Ergostanol* (XXVI).—The 9 : 22-diene (70 mg.) in acetic acid (5 c.c.) was shaken with hydrogen and Adams's catalyst (50 mg.) until absorption ceased (1 hr.). The solution was filtered and evaporated to dryness, and the noncrystalline acetate hydrolysed with hot methanolic potash. Crystallisation from methanol gave 14β-*ergostanol* (27 mg.) as needles, m. p. 114—116°, $[\alpha]_D$ +47° (Found : C, 83·5; H, 12·4. $C_{28}H_{50}O$ requires C, 83·5; H, 12·5%).

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