Reactions of Steroid A-ring Lactones with Grignard Reagents

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The addition of solutions of Grignard reagents to 4-oxacholesta-5,7-dien-3-one (4) yields the bridged ketones, 3-alkyl-3-hydroxy-3(5 → 6βH)*abeo*-A-norcholest-7-en-5-ones (12) as well as 'over-reacted' products which are formed from the latter by reduction (as against Grignard addition) at the 5-carbonyl group. 4-Oxacholest-5-en-3-one (1) behaves similarly when treated with isopropylmagnesium bromide. Both 3-hydroxy-3-isopropyl-3(5 → 6βH)*abeo*-A-norcholestan-5-one and the isomeric diketone, 3-isopropyl-3,5-seco-A-norcholestan-3,5-dione (16) on contact with toluene-*p*-sulphonic acid in benzene give, in part, 4,4-*dimethylcholest*-5-en-3-one which is further converted into a mixture of aromatic hydrocarbons rich in 1,3,4-trimethyl-19-norcholest-1,3,5(10)-triene (25).

The reaction of lactones of type (1) with the Grignard reagents of primary halides is well documented and has been much used in steroid and terpene synthesis;[1] the initial adducts[2] are of type (2) and yield αβ-unsaturated ketones (3) on treatment with alkali-metal hydroxides or alkoxides. If the configuration at C-10 is unnatural the yield of ketone (3) is low, the original lactone being recovered along with 'over-reacted' material.[1b] With an excess of Grignard reagent lactones of natural configuration also give 'over-reacted' products and structures have been assigned to some of these.[3] This paper records, in the main, the behaviour of the lactone (4) with methyl and ethyl Grignard reagents and of the lactones (1)[4] and (4) with isopropyl Grignard reagent.

The synthesis of the lactone (4) was achieved by two routes. Bromination of the acid (5; R = H) has been reported by Windaus[5] to give a monobromo-derivative, m.p. 154—156°. In our hands the yield of this compound was low. A substance of approximately the same melting point (40% yield) was obtained by bromination in chloroform, the ^{1}H n.m.r. spectrum of which had peaks at τ 5·00 and 5·58 (relative intensity 85 : 15) evidently due[6] to the 6β- and 6α-hydrogens of the bromo-keto-acids (6; R = H) and (7; R = H). When the hydrogen bromide formed in the reaction was kept at a low but constant level ('kinetic control'[7]) the product was a mixture (25 : 75) of the same two acids in 85% yield.

Bromination of the ester (5; R = Me) in chloroform gave a mixture of esters (6; R = Me) and (7; R = Me) but under 'kinetic control'[7] the 6β-bromo-ester (7; R = Me) was readily obtained. The u.v. ($n \rightarrow \pi^*$ carbonyl),[8] i.r. (carbonyl stretching),[9] and ^{1}H n.m.r. (CO–CHBr and 10Me)[6,10] spectra are consistent only for an axial conformation of the bromine atom. The pronounced negative dichroic absorption ($\Delta\varepsilon$ — 2·41) at 326 nm establishes a β-configuration (ring B chair) rather than an α-configuration (ring B-boat).[11] After adsorption on alumina the above bromo-ester gave three compounds. The first proved to be the 6α-bromo-ester (6; R = Me) (see Table), the second the unbrominated ester (5). The third compound, $C_{27}H_{44}O_4$ had $\lambda_{max.}$ (ethanol) 273 nm (ε 9200) and gave an intense purple-red colour with methanolic ferric chloride. Its i.r. spectrum had bands at 3370 (OH), 1720 (ester),

[1] (*a*) G. I. Fujimoto, *J. Amer. Chem. Soc.*, 1951, **73**, 1856; R. D. H. Heard and P. Ziegler, *ibid.*, 1951, **73**, 4036; B. Belleau, *ibid.*, 1951, **73**, 5441: (*b*) R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler, and W. M. MacLamore, *J. Amer. Chem. Soc.*, 1952, **74**, 4223: (*c*) P. Wieland, H. Ueberwasser, G. Anner and K. Miescher, *Helv. Chim. Acta*, 1953, **36**, 1231; E. J. Corey, H.-J. Hess and S. Proskow, *J. Amer. Chem. Soc.*, 1959, **81**, 5258; L. Velluz, G. Norniné, G. Amiard, V. Torelli, and J. Cérède, *Compt. rend.*, 1963, **257**, 3086.

[2] G. I. Fujimoto and K. D. Zwahlen, *J. Org. Chem.*, 1960, **25**, 445; S. A. Julia, A. Eschenmoser, H. Heusser, and N. Tarköy, *Helv. Chim. Acta*, 1953, **36**, 1885.

[3] F. Sondheimer and Y. Mazur, *J. Amer. Chem. Soc.*, 1957, **79**, 2906.

[4] R. B. Turner, *J. Amer. Chem. Soc.*, 1950, **72**, 579.

[5] A. Windaus, *Ber.*, 1906, **39**, 2008.

[6] A. Nickon, M. A. Castle, R. Harada, C. E. Berkoff, and R. O. Williams, *J. Amer. Chem. Soc.*, 1963, **85**, 2185.

[7] *Inter alia*, E. J. Corey, *Experientia*, 1953, **9**, 329; *J. Amer. Chem. Soc.*, 1954, **76**, 175.

[8] R. C. Cookson, *J. Chem. Soc.*, 1954, **282**.

[9] R. N. Jones, D. A. Ramsay, F. Herling, and K. Dobriner, *J. Amer. Chem. Soc.*, 1952, **74**, 2828.

[10] R. F. Zürcher, *Helv. chim. Acta*, 1963, **46**, 2054.

[11] C. Djerassi and W. Klyne, *J. Amer. Chem. Soc.*, 1957, **79**, 1506.

and 1670 cm^{-1} (αβ-unsaturated carbonyl) and the ^1H n.m.r. spectrum had a doublet (J 2·5 Hz, 1H) at τ 3·97. This compound must therefore be the diosphenol (8; R = Me).

Attempted dehydrobromination of the 1 : 3 mixture of 6α- and 6β-bromo-acids (6; R = H) and (7; R = H), with potassium t-butoxide in t-butyl alcohol under nitrogen gave a product which after treatment with diazomethane and chromatography on alumina gave, along with unbrominated ester (5), the diosphenol (8; R = Me) identical with the previous compound; u.v. examination of the crude product showed the yield to be as high as 40%. The formation of diosphenols from dibromoketo-steroids, *e.g.* 2α,4α-dibromocholestan-3-one,[12] is well known and can be rationalised by displacements of type (9). As far as we know this is the first example of the formation of such a compound from a monobromo-ketone and mechanism (10) is suggested for this. Dehydrobromination of the same bromo-acid mixture with lithium bromide–lithium carbonate in dimethylformamide[13] gave, in up to 97% yield, the desired unsaturated acid (11; R = H) which underwent smooth cyclisation (54%) to the diene lactone (4). The ^1H n.m.r. spectrum of this compound was of interest in that in deuteriochloroform (but not in deuteriobenzene) the C-6 and C-7 proton resonances coincided.

The second route to the diene lactone (4) lay in allylic bromination—dehydrobromination of the lactone (1). With *N*-bromosuccinimide in carbon tetrachloride hydrogen bromide was evolved and the product was the acid (11; R = H). When the lactone was treated *N*-bromosuccinimide in the presence of epichlorohydrin[14] the lactone (4) was produced directly in 58% yield. The overall yield from cholest-4-en-3-one by either route was *ca.* 25%.

Treatment of the lactone (4) with 1 molar equivalent of methylmagnesium iodide in ether gave the ketol (12; R = Me), the structure of which follows from its ^1H n.m.r. spectrum (see Table). Double irradiation at τ 4·75 collapsed the doublet at τ 7·28 (J 6 Hz, 6-H) to a singlet. Sodium methoxide in methanol converted

TABLE

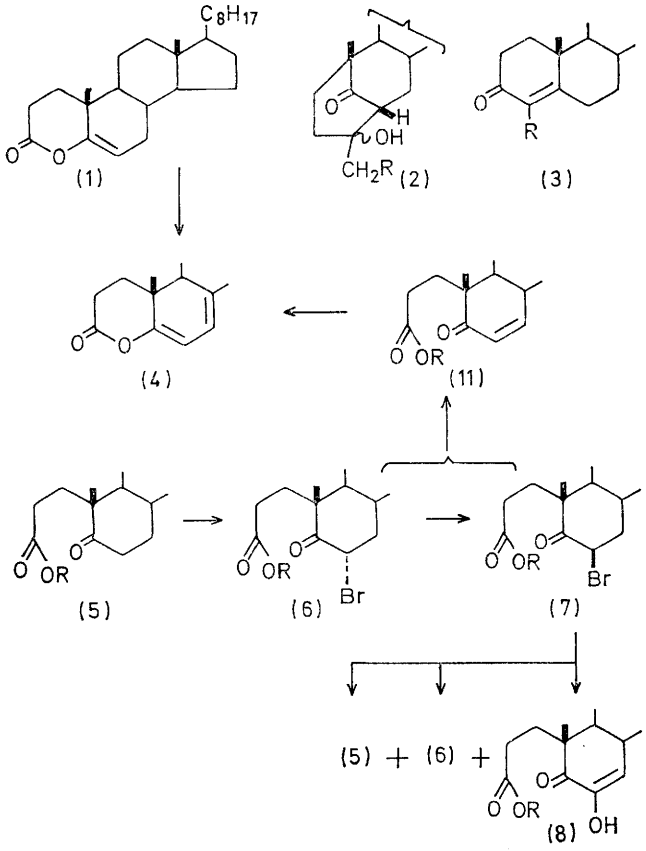
Compound	$\lambda_{max.}$ (nm) (ε)	$\nu_{max.}$ (cm^{-1})		τ
4-Oxacholesta-5,7-dien-3-one (4), m.p. 120°	(Ethanol) 281 (10,900)	(KBr) 1783, 1749, 1666, 1168	($CDCl_3$)	9·35 (13-Me), 8·87 (10-Me), 4·49 (6-H and 7-H)
			(C_6D_6)	9·44 (13-Me), 9·17 (10-Me), 4·65 (m) (7-H), 4·48 (d, J 6·5 Hz) (6-H)
Methyl 5-oxo-3,5-secocholestan-3-oate (5; R = Me)	(Ether) 292 (24)	($CHCl_3$) 1733, 1703, 1440, 1176	($CDCl_3$)	9·25 (13-Me), 8·89 (10-Me)
Methyl 6α-bromo-5-oxo-3,5-secocholestan-3-oate (6; R = Me), m.p. 70·5°	(Ether) 291 (35)	($CHCl_3$) 1727, 1448, 1177	($CDCl_3$)	9·26 (13-Me), 8·83 (10-Me), 5·00 (dd, J 6, 12·5 Hz) (6β-H)
Methyl 6β-bromo-5-oxo-3,5-secocholestan-3-oate (7; R = Me), m.p. 101—101·5°	(Ether) 325 (105)	($CHCl_3$) 1732, 1703, 1177	($CDCl_3$)	9·22 (13-Me), 8·59 (10-Me), 5·57 (m) (6α-H)
Methyl 6-hydroxy-5-oxo-3,5-secocholest-6-en-3-oate (8; R = Me), m.p. 112—113°	(Ethanol) 273 (9500)	(KBr) 3370, 1718, 1670	($CDCl_3$)	9·23 (13-Me), 8·92 (10-Me), 3·97 (d, J 2·5 Hz) (7-H)
5-Oxo-3,5-secocholest-6-en-3-oic acid (11; R = H)	(Ethanol) 234 (7650)	(CCl_4) 1711, 1678	($CDCl_3$)	9·23 (13-Me), 8·96 (10-Me), 4·05 (dd, J 2·5, 10 Hz) (7-H), 3·15 (d, J 10 Hz) (6-H)
3-Methyl-3-hydroxy-3(5 ⟶ 6βH)-*abeo*-A-norcholest-7-en-5-one (12; R = Me), m.p. 141°		(CCl_4) 3460, 1722, 1093, 912	($CDCl_3$)	9·53 (13-Me), 8·99 (10-Me), 8·74 (3-Me), 7·28 (d, J 6 Hz) (6-H), 4·75 (d, J 6 Hz) (7-H)
3-Ethyl-3-hydroxy-3(5 ⟶ 6βH)-*abeo*-A-norcholest-7-en-5-one (12; R = Et), m.p. 143·5—144°		(KBr) 3440, 1706, 1279, 990	($CDCl_3$)	9·55 (13-Me), 8·99 (10-Me), 7·22 (d, J 6 Hz) (6-H), 4·79 (complex doublet, J 6 Hz), (7-H)
3-Isopropyl-3-hydroxy-3(5 ⟶ 6βH)-*abeo*-A-norcholest-7-en-5-one 12; R = Pr^i), m.p. 134 and 144°	(Ethanol) 290 (97)	(CCl_4) 3620, 3505, 1720, 1117, 249	($CDCl_3$)	9·55 (13-Me), 8·99 (10-Me), 7·12 (d, J 6 Hz) (6-H), 4·84 (d, J 6 Hz) (7-H)
3-Ethyl-3-hydroxy-3(5 ⟶ 6βH)-*abeo*-A-norcholest-7-en-5-ol (14; R = Et), m.p. 173—174°		(KBr) 3325, 1447, 1173, 1057	($CDCl_3$)	9·48 (13-Me), 9·02 (10-Me), 7·75 (m) (6-H), 6·16 (d, J 3 Hz) (5-H), 4·85 (complex doublet, J 6·5 Hz) (7-H)
3-Hydroxy-3-isopropyl-3(5 ⟶ 6βH)-*abeo*-A-norcholest-7-en-5-ol (14; R = Pr^i), m.p. 180°		(CCl_4) 3510, 1067, 1028, 954	($CDCl_3$)	9·48 (13-Me), 9·03 (10-Me), 7·42 (dd, J 3·6, 7·2 Hz) (6-H), 6·19 (d, J 3·6 Hz) (5-H), 4·88 (d, J 7·2 Hz) (7-H)
3-Hydroxy-3-isopropyl-3(5 ⟶ 6βH)-*abeo*-A-norcholestan-5-one (15), m.p. 158·5—159·5°	(Ethanol) 290 (35)	(CCl_4) 3600, 3480, 1707, 1158, 1094	($CDCl_3$)	9·39 (13-Me), 9·02 (probably 10-Me), 9·20, 9·12, 9·10 (methyls), 7·42 (complex doublet) (6-H)
3-Hydroxy-3-isopropyl-3(5 ⟶ 6βH)-*obeo*-A-norcholestan-5-ol (22), m.p. 212—214°		(KBr) 3180, 1025, 948	($CDCl_3$)	9·35 (13-Me), 9·24, 9·20, 9·10, 9·04 (methyls), 6·18 (complex doublet, J 5 Hz) (5-H)

[12] A. Butenandt, G. Schramm, A. Wolff, and H. Kudszus, *Ber.*, 1936, **69**, 2779.

[13] R. Joly and J. Warnant, *Bull. Soc. chim. France*, 1958, 367; R. P. Holysz, *J. Amer. Chem. Soc.*, 1953, **75**, 4432.

[14] M. P. Hartshorn and Sir E. R. H. Jones, *J. Chem. Soc.*, 1962, 1312; D. N. Kirk, D. K. Patel, and V. Petrow, *ibid.*, 1956, 627.

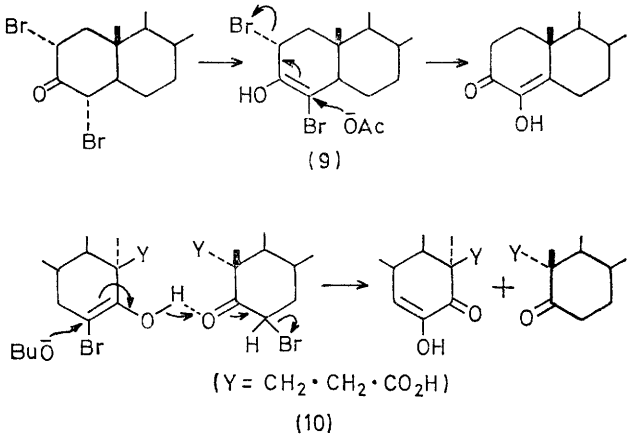
the compound into cholesta-4,6-dien-3-one (13; R = H) identical with an authentic specimen.[15]

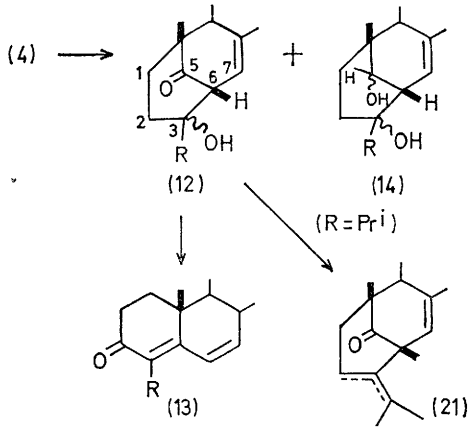


The action of 1 molar equivalent of ethylmagnesium bromide on compound (4) gave a mixture (*ca.* 1 : 1) of the ketol (12; R = Et) and its dihydro-derivative (14; R = Et). Use of 2 molar equivalents of Grignard reagent gave the same compounds in the ratio 1 : 2. The mixture on treatment with chromium trioxide–pyridine [16] gave the ketol (12; R = Et); with methanolic sodium methoxide it gave a readily separable mixture of the diol (14; R = Et) and 4-methylcholesta-4,6-dien-3-one (13; R = Me), m.p. 77°. The latter has been obtained previously [17] as an oil. Assignment of structure (14; R = Et) to the diol is based on its ^{1}H n.m.r. spectrum and its oxidation to the ketol (12; R = Et).

The reaction between the diene lactone (4) and isopropylmagnesium bromide (1 mol. equiv.) in ether gave (25%) the diol (14; R = Pr^i). T.l.c. showed almost complete absence of the ketol (12; R = Pr^i). With 2 molar equivalents of Grignard reagent the yield increased to 45%. Oxidation to the ketol (12; R = Pr^i) was readily achieved by chromium-trioxide–pyridine but not by either chromium trioxide–acetone or by the Oppenauer method.

Initial difficulties encountered in the reaction between isopropylmagnesium bromide and the lactone (1) led us to seek the preparation of the ketol (15) by way of the diketone (16). 4,4-Dimethylcholest-5-en-3-one [18] (17) was reduced catalytically according to the directions of Atwater [19] except for the presence of perchloric as against hydrochloric acid, but in our hands the carbonyl group only was reduced, the product being 4,4-dimethylcholest-5-en-3β-ol (78%) identical with an authentic [18] specimen. To reduce this compound further





a high-pressure procedure [20] was necessary. Ring contraction of the product with phosphorus pentachloride then gave 3-isopropylidene-A-nor-5α-cholestane isomerised to 3-isopropyl-A-norcholest-3(5)-ene (18) (80%) by hydrochloric acid,[21] but not, in our experience by trichloroacetic acid.[20] Compound (18) was chromatographically homogeneous; it was of sharp but lower melting point (56°) than that (96—99°) of the compound previously reported [20,22] and was somewhat more dextrorotatory ([α]$_D$ +58°); the ^{1}H n.m.r. spectrum

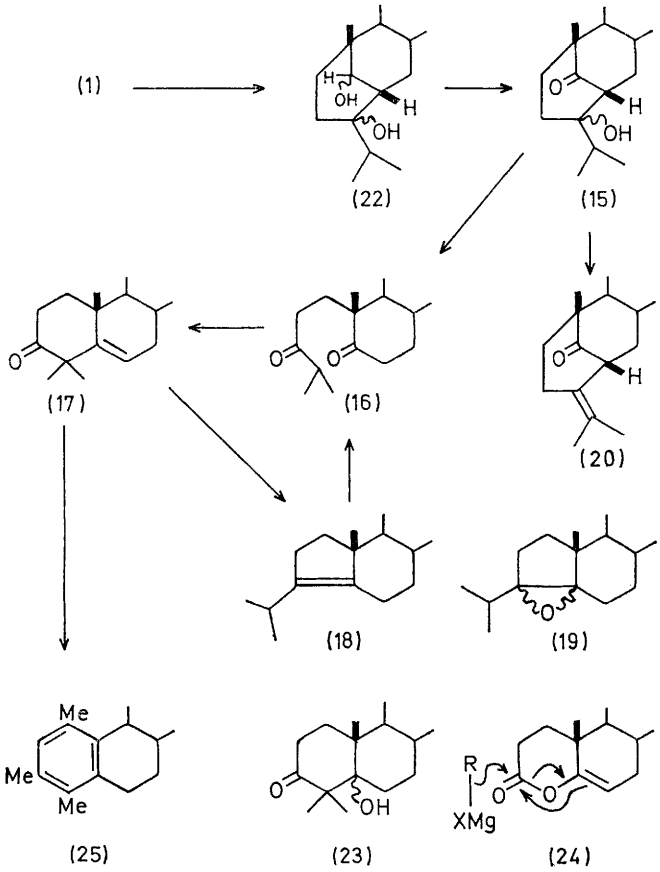
[15] A. L. Wilds and C. Djerassi, *J. Amer. Chem. Soc.*, 1946, **68**, 1712.
[16] G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Amer. Chem. Soc.*, 1953, **75**, 422.
[17] J. M. Coxon, M. P. Hartshorn, and D. N. Kirk, *Tetrahedron*, 1964, **20**, 2531.
[18] R. B. Woodward, A. A. Patchett, D. H. R. Barton, D. A. J. Ives, and R. B. Kelly, *J. Chem. Soc.*, 1957, 1131.
[19] N. W. Atwater, *J. Amer. Chem. Soc.*, 1960, **82**, 2847.
[20] J.-F. Biellmann and G. Ourisson, *Bull. Soc. chim. France*, 1962, 331.
[21] G. R. Pettit and B. Green, *J. Org. Chem.*, 1961, **26**, 4673.
[22] F. Cohen and R. Stevenson, *J. Org. Chem.*, 1965, **30**, 2268.

showed neither olefin-bound hydrogen nor methyl. When the compound was ozonised and the product worked-up with zinc and acetic acid it yielded the epoxide (19) (7%) and the diketone (16) (77%). The latter was smoothly cyclised by mesitylmagnesium bromide in ether to the ketol (15). The converse reaction, (15) ⟶ (16), was brought about quantitatively with methanolic sodium methoxide. A similar attempt to open the ketol ring in (12; R = Pr^i) was not successful; use of more powerful bases on this compound brought about complex changes which were not elucidated. The ketol (15) was readily dehydrated to the isopropylidene ketone (20); by contrast the unsaturated analogue (12; R = Pr^i) gave a mixture of isopropyl and isopropylidene compounds (21). Enhanced $n \rightarrow \pi^*$ carbonyl absorption was found for the compounds (20), the mixture (21), and to a lesser extent the ketol (12; R = Pr^i) and is evidently connected [23] with the geometry of the unsaturated centres in these molecules. The 13-methyl resonance in compound (12; R = Pr^i) was considerably further upfield (τ 9·55) than that (τ 9·39) in compound (15).

The reaction between the lactone (1) and isopropylmagnesium bromide was carried out initially in tetrahydrofuran and gave as main product a compound (20—37%), m.p. 56° which was eventually shown to be the ester (5; R = Pr^i). With ether as solvent this compound was not formed; compounds (15) and (22) were obtained together (44%) in one chromatographic fraction and oxidation of the mixture (chromium trioxide–acetone was effective in this case) gave the ketol (15) identical with the previous compound.

In all cases studied so far the action of Grignard reagents on the lactones has given compounds such as (15) rather than (23). The reaction can be rationalised as in (24); the isopropyl ester mentioned earlier presumably arises by a similar mechanism, *i.e.* attack of isopropyloxymagnesium bromide (obtained by the action of atmospheric oxygen on the Grignard reagent) except for the formation of the C(6)–C(3) bond and reflects the differing electron density at C(3) brought about by attachment of alkoxy as against alkyl. The steric nature of R (24) evidently does not influence the course of the reaction. The mesitylmagnesium bromide cyclisation, (16) ⟶ (15), is brought about by proton abstraction from C-6.

When the diketone (16) was heated with toluene-*p*-sulphonic acid in benzene for 3 h the products consisted of unchanged diketone, a hydrocarbon fraction, a compound, m.p. 79—80°, and 4,4-dimethylcholest-5-en-3-one (17). The same products and one other, m.p. 125—126°, were produced from the ketol (15). When the time of contact was 36 h, only the hydrocarbon fraction (70%) was found. The chromatographic and spectroscopic (particularly ^{1}H n.m.r.) properties were consistent with this material being a mixture of two isomeric trimethyl-19-norcholesta-1,3,5(10)-trienes. With some labour the major product was separated and proved to be identical with 1,3,4-trimethyl-19-norcholesta-1,3,5(10)-triene (25) which was prepared [24,25] and independently synthesised [24] during the course of this work. The compound is formed from 4,4-dimethylcholest-5-en-3-one under acid conditions [24,25] and the probable mechanism for this reaction has been discussed.[26] The present work establishes its formation by the sequence (15) ⟶ (16) ⟶ (17) ⟶ (25).



EXPERIMENTAL

All evaporations were carried out at reduced pressure. Optical rotations were measured on chloroform solutions at 15° and ^{1}H n.m.r. spectra were taken in deuteriochloroform.

Alumina for chromatography was neutral and of Brockmann Activity I; alumina (3% H_2O) and alumina (6% H_2O) refer to this material which had been deactivated by the addition of 3 and 6% by weight of water. Silica gel GF 254 (E. Merck A.G., Darmstadt) was used for thin layer and preparative layer chromatography. Chromatograms were developed with light petroleum (b.p. 40—60°)–benzene–ether mixtures; 50% aqueous sulphuric acid or 5% phosphomolybdic acid in 95% ethanol were used occasionally as sprays for visual detection. Silica gel (5% $AgNO_3$) refers to silica gel impregnated with 5%

[23] E. Bunnenberg, C. Djerassi, K. Mislow, and A. Moscowitz, *J. Amer. Chem. Soc.*, 1962, **84**, 2823; S. F. Mason, *Quart. Rev.*, 1961, **15**, 309: J. N. Murrell, 'The Theory of the Electronic Spectra of Organic Molecules,' Methuen, London, 1963, p. 165.

[24] Y. Sato, A. Mizugushi, S. Tanaka, and K. Tsuda, *Chem. and Pharm. Bull.* (*Japan*), 1965, **13**, 393.

[25] P. Bey, F. Lederer, and G. Ourisson, *Chem. and Pharm. Bull.* (*Japan*), 1965, **13**, 1138.

[26] P. Bey and G. Ourisson, *Bull. Soc. chim. France*, 1968, 1411.

by weight of silver nitrate. Light petroleum generally refers to material b.p. 40—60°.

5-Oxo-3,5-secocholestan-3-oic acid (5; R = H).—Cholest-4-en-3-one [27] (30 g) in dichloromethane (300 ml) and methanol (300 ml) was treated with ozonised oxygen at −78° until a permanent blue colour developed. The solution was poured into water (100 ml) containing hydrogen peroxide (15 ml; 100 volume) and the mixture was stirred overnight. The organic phase was dried and evaporated, the residue dissolved in ether, and the acid extracted into 1% aqueous potassium hydroxide. The aqueous phase was acidified and extracted with ethyl acetate to give the keto-acid (5; R = H) (21·8 g, 70%), m.p. 150—151° (from ether–light petroleum) (lit.,[4] 151·5—152·5°), $[\alpha]_D$ +34°, $\lambda_{max.}$ (ether) 296 nm (ε 30), $\nu_{max.}$ ($CHCl_3$) 1705 cm^{-1}; τ 9·27 (13-Me) and 8·88 (10-Me).

6α- and 6β-Bromo-5-oxo-3,5-secocholestan-3-oic Acids (6; R = H) and (7; R = H).—(*a*) The keto-acid (30 g) in carbon tetrachloride (1000 ml) containing acetic acid (50 ml) was treated with hydrogen bromide in acetic acid (50% w/v; 1 ml). To the cold (0°) stirred solution was added dropwise during 3 h a solution of bromine (12·5 g) in acetic acid (400 ml) containing anhydrous sodium acetate (6·4 g). After a further 2 h the solution was washed with water and sodium thiosulphate solution, and then dried and evaporated. The mixed acids (31·2 g, 85%) had m.p. 106—114° (from light petroleum), $[\alpha]_D$ −57°; τ 5·01 (6β-H) and 5·56 (6β-H) (combined intensity, 1H) (ratio 1 : 3) (Found: C, 64·81; H, 8·8. $C_{26}H_{43}BrO_3$ requires C, 64·6; H, 8·95%).

(*b*) The mixture of bromo-acids (1 g) was heated under reflux with benzene (100 ml) containing toluene-*p*-sulphonic acid (1 g) for 10 h. Work-up gave a solid, m.p. 146—148° which after four crystallisations from aqueous alcohol furnished *6α-bromo-5-oxo-3,5-secocholestan-3-oic acid* (6; R = H), m.p. 154—156°, $[\alpha]_D$ +6°; $\lambda_{max.}$ (ether) 292 nm (ε 25); $\nu_{max.}$ ($CHCl_3$) 1721, 1716 cm^{-1}; τ, 9·24 (13-Me), 8·83 (10-Me), and 5·00 (6β-H) (Found: Br, 16·55. $C_{26}H_{43}BrO_3$ requires Br, 16·55%).

Methyl 5-oxo-3,5-secocholestan-3-oate (5; R = Me) [4] was prepared by dissolving the keto-acid (16 g) in methanol (160 ml), dichloromethane (30 ml), and concentrated hydrochloric acid (4 ml). After 24 h work-up gave an oil (16 g, 96%), $[\alpha]_D$ +35°; c.d. $\lambda_{max.}$ 301 nm (Δε + 0·40).

Isopropyl 5-Oxo-3,5-secocholestan-3-oate. This compound was prepared similarly and had m.p. 56·5°; $\nu_{max.}$ (KBr) 1732 and 1701; τ 9·26 (13-Me) and 8·88 (10-Me) (Found: C, 77·5, H, 11·05. $C_{29}H_{50}O_3$ requires C, 77·95; H, 11·3%). The *2,4-dinitrophenylhydrazone* had m.p. 141—142° (from ethanol), $\lambda_{max.}$ ($CHCl_3$) 368 nm (ε 22,000); $\nu_{max.}$ (KBr) 1730 cm^{-1} (Found: C, 67·45; H, 8·85; N, 8·95. $C_{35}H_{54}N_4O_6$ requires C, 67·05; H, 8·7; N, 8·95%).

Methyl 6β-Bromo-5-oxo-3,5-secocholestan-3-oate (7; R = Me).—Bromine (9·60 g) was added to a solution of anhydrous sodium acetate (4·92 g) in a mixture of carbon tetrachloride and acetic acid (1 : 4; v/v) and the solution was made up to 500 ml. To a stirred solution of the methyl ester (above) (10 g) in carbon tetrachloride (100 ml) at 0° was added 0·01M-hydrogen bromide in acetic acid (10 ml) and then dropwise, during 3 h, 200 ml. of the bromine solution. The solution when washed with water, dried, and evaporated gave the crystalline *bromo-ester* (7; R = Me) (4·2 g, 35%), m.p. 101—101·5° (from di-isopropyl ether), $[\alpha]_D$ −83°; c.d. $\lambda_{max.}$ 326 nm (Δε − 2·41) (Found: C, 65·05; H, 8·95; Br, 16·1. $C_{27}H_{45}BrO_3$ requires C, 65·2; H, 9·05; Br, 16·1%).

Methyl 6α-Bromo-5-oxo-3,5-secocholestan-3-oate (6; R = Me).—The 6β-bromo-ester (1 g) was dissolved in benzene and applied to alumina (6% H_2O) (30 g). After 24 h elution with benzene gave an oil (560 mg) which was separated by chromatography (light petroleum–benzene) on alumina (6% H_2O) into *methyl 6α-bromo-5-oxo-3,5-secocholestan-3-oate* (210 mg), m.p. 70·5° (from di-isopropyl ether), c.d. $\lambda_{max.}$ (ether) 274 (Δε + 0·12) and 307 nm (Δε − 0·30), $[\alpha]_D$ +11° (Found: C, 65·0; H, 9·2; Br, 16·0. $C_{27}H_{45}BrO_3$ requires C, 65·2; H, 9·05; Br, 16·1%) and methyl 5-oxo-3,5-secocholestan-3-oate (120 mg) (5; R = Me).

Elution with ether gave (90 mg) *methyl 6-hydroxy-3,5-seco-5-oxocholest-6-en-3-oate,* (8; R = Me), m.p. 112—113° (from di-isopropyl ether), $[\alpha]_D$ −80° (Found: C, 75·05; H, 10·25. $C_{27}H_{44}O_4$ requires C, 74·95; H, 10·25%).

Dehydrobromination Experiments.—(*a*) The mixture (1 : 3) of 6α- and 6β-bromo-acids (5 g) was dissolved in anhydrous t-butyl alcohol (100 ml) containing potassium-t-butoxide (from 2 g of potassium) at 20° under nitrogen. The solution immediately became yellow. After 12 h the solution was diluted with ether and washed with dilute hydrochloric acid and water, and then dried and evaporated. The glass-like product, $\lambda_{max.}$ (ethanol) 275 nm, $E^{1\%}_{1cm}$ 86, was treated with an excess of diazomethane in ether and the product was chromatographed on alumina (6% H_2O) (150 g). The benzene eluates furnished (5; R = Me), chromatographically identical with authentic material. The ether eluates gave methyl 6-hydroxy-3,5-seco-5-oxocholest-6-en-3-oate (8; R = Me), m.p. 112—113°, identical with the compound described above.

(*b*) The mixture of acids (8·8 g) in dimethylformamide (100 ml), lithium bromide (10 g), and lithium carbonate (10 g) was stirred at 110° for 6 h under nitrogen. The cooled mixture was diluted with ether, washed with dilute hydrochloric acid and water and then dried and evaporated, to give 3,5-seco-5-oxocholest-6-en-3-oic acid (11; R = H) as a glass (7·1 g, 97%).

This compound (1 g) was esterified with diazomethane in ether and the ester purified on alumina (6% H_2O) and (p.l.c.) on silica gel to give *methyl 5-oxo-3,5-secocholest-6-en-3-oate* (11; R = Me) as an oil, $\lambda_{max.}$ (ethanol) 234 nm (ε 8600); $[\alpha]_D$ −64°; $\nu_{max.}$ (CCl_4) 1739, 1707, and 1676 cm^{-1}; τ 9·23 (13-Me) and 3·16 (dd, *J* 10·5, 1·5 Hz) (6-H) (Found: C, 77·7; H, 10·9. $C_{27}H_{42}O_3$ requires C, 77·83; H, 10·65%).

4-Oxacholest-5-en-3-one (1) was prepared by heating the acid (5; R = H) (30 g) with toluene-*p*-sulphonic acid (3 g) in pure acetic anhydride (300 ml) for 3 h at 90°. The cooled mixture was diluted with ether, washed rapidly with saturated aqueous sodium hydrogen carbonate and water, and then dried and evaporated. The lactone (1) (19 g, 66%) had m.p. 92—93° (from di-isopropyl ether) (lit.,[4] 94—94·5°), τ 9·30 (13-Me), 8·90 (10-Me), and 4·74 (complex d, *J* 4·2 Hz).

4-Oxacholesta-5,7-dien-3-one (4).—(*a*) A solution of the acid (11; R = H) (20 g) in acetic anhydride (175 ml) was heated with toluene-*p*-sulphonic acid (2 g) on a water-bath for 2 h. The cooled mixture was diluted with ether and washed with saturated aqueous sodium hydrogen carbonate and water and then dried and evaporated to yield *4-oxacholesta-5,7-dien-3-one* (4), (10·4 g, 54%), m.p. 113—116°. An analytical specimen had m.p. 120° (from di-isopropyl ether), $[\alpha]_D$ −96·5° (Found: C, 81·0; H, 10·4. $C_{26}H_{40}O_2$ requires C, 81·2; H, 10·5%).

[27] J. F. Eastham and R. Teranishi, *Org. Synth.*, 1955, **35**, 39.

(*b*) 4-Oxacholest-5-en-3-one (1) (5 g), *N*-bromosuccinimide (2·5 g), epichlorohydrin (5 ml), and carbon tetrachloride (250 ml) were heated under reflux for 6 h. The residue left on evaporation was crystallised from light petroleum–di-isopropyl ether and gave the same compound (2·9 g, 58%), m.p. 114—116°, as in the previous experiment.

3-*Hydroxy*-3-*methyl*-3(5 ⟶ 6β H)abeo-A-*norcholest*-7-*en*-5-*one* (12; R = Me).—A stock solution of methylmagnesium iodide (10 ml; 0·32M; 10% excess) in ether was added during 15 min to a stirred solution of the lactone (4) (1·15 g) in anhydrous ether (30 ml). After 1 h the solution was worked up by washing it with dilute hydrochloric acid, water, and dilute sodium thiosulphate solution followed by drying and evaporation. The residue in benzene was applied to alumina (6% H_2O). The benzene–ether eluates afforded *compound* (12; R = Me) (0·25 g, 21%), m.p. 141° (from di-isopropyl ether), $[\alpha]_D$ +120° (Found: C, 80·9; H, 11·15. $C_{27}H_{44}O_2$ requires C, 80·95; H, 11·05%).

The compound above (230 mg) was heated under reflux for 6 h with a solution of sodium (250 mg) in anhydrous methanol (25 ml) under nitrogen. Work-up gave (150 mg) cholesta-4,6-dien-3-one (13; R = H), m.p. 80—80·5° (from di-isopropyl ether–methanol), identical with an authentic specimen,[15] $\nu_{max.}$ (KBr) 1661, 1615, and 877 cm^{-1}. The 2,4-dinitrophenylhydrazone had m.p. 189—190°, $\lambda_{max.}$ ($CHCl_3$) 310 (ε 14,200) and 402 nm (ε 35,000).

3-*Ethyl*-3-*hydroxy*-3(5 ⟶ 6β H)abeo-A-*norcholest*-7-*en*-3-*one* (12; R = Et).—A stock solution of ethylmagnesium iodide in ether (56 ml; 0·22M; 20% excess) was added to a vigorously stirred solution of the lactone (4) (5 g) in ether (150 ml) during 15 min. After 18 h work-up as for (9; R = Me) gave a crystalline solid (2·12 g, 40%), m.p. 144—148° (from di-isopropyl ether). The relative intensities of the (^1H n.m.r.) two 13-methyl groups (see Table) indicated a 60 : 40 ratio for compounds (12; R = Et) and (14; R = Et) respectively. Use of 110% excess of Grignard reagent gave (45%) a 35 : 65 mixture, m.p. 150—152°, of the same two compounds.

The mixture (720 mg) in pure pyridine (8 ml) was added to a well stirred solution of chromium trioxide (600 mg) in pyridine (6 ml). After 12 h it was poured into water and extracted with light petroleum. Work-up gave compound (12; R = Et) (460 mg, 64%), m.p. 143·5—144° (from di-isopropyl ether), $[\alpha]_D$ +112° (Found: C, 81·55; H, 11·0. $C_{28}H_{46}O_2$ requires C, 81·1, H, 11·2%).

3-*Ethyl*-3-*hydroxy*-3(5 ⟶ 6β H)abeo-A-*norcholest*-7-*en*-5-*ol* (14; R = Et) *and* 4-*Methylcholesta*-4,6-*dien*-3-*one* (13; R = Me).—The 35 : 65 ketol–diol mixture (1·0 g) was dissolved in a solution of sodium (1·0 g) in anhydrous methanol (50 ml) and the mixture was heated under reflux for 12 h under nitrogen. The cooled mixture was diluted with ether, washed with water, and then dried and evaporated. P.l.c. gave from the uppermost band an oil (300 mg) and from the lower band (both bands conveniently detected by a phosphomolybdic acid spray) a crystalline solid (320 mg). The oil furnished 4-methylcholesta-4,6-dien-3-one (13; R = Me) (140 mg), m.p. 76—77° (from di-isopropyl ether–methanol), $\lambda_{max.}$ (ethanol) 292 nm (s 26,000); $[\alpha]_D$ +89°; $\nu_{max.}$ (KBr) 1667, 1617, 1322, and 782 cm^{-1}; τ 9·23 (13-Me), 8·92 (10-Me), 8·16 (4-Me), 3·84 (d, *J* 11 Hz, 6-H and 3·47 (dd, *J* 11, 2·5 Hz, 7-H) (Found: C, 84·8; H, 11·15. Calc. for $C_{28}H_{44}O$: C, 84·8; H, 11·2%). The 2,4-dinitrophenylhydrazone had m.p. 256°, $\lambda_{max.}$ ($CHCl_3$) 315 (ε 15,000) and 407 nm (ε 34,000).

The crystalline solid gave 3-*ethyl*-3-*hydroxy*-3(5 ⟶ 6β H)-abeo-A-*norcholest*-7-*en*-5-*ol* (14; R = Et) (190 mg), m.p. 173—174° (from di-isopropyl ether), $[\alpha]_D$ +155° (Found: C, 80·35; H, 11·25. $C_{28}H_{48}O_2$ requires C, 80·7; H, 11·6%).

3-*Hydroxy*-3-*isopropyl*-3(5 ⟶ 6β H)abeo-A-*norcholest*-7-*en*-5-*ol* (14; R = Pr^i).—A stock solution of isopropylmagnesium bromide in ether (135 ml; 0·83M; 120% excess) was added during 15 min. to a well-stirred solution of the lactone (4) (20 g) in ether (500 ml). After 12 h the product was worked up as for (12; R = Me). Crystallisation gave 7·95 g and chromatography (benzene → ether on alumina, 6% H_2O) of the material in the mother liquors afforded a further 2·2 g (total 10·15 g, 45%) of *compound* (14; R = Pr^i), m.p. 180° (from di-isopropyl ether) (Found: C, 81·1; H, 11·55. $C_{29}H_{50}O_2$ requires C, 80·85; H, 11·7%).

3-*Hydroxy*-3-*isopropyl*-3(5 ⟶ 6β H)abeo-A-*norcholest*-7-*en*-5-*one* (12; R = Pr^i).—To a stirred solution of crystallised chromium trioxide (9 g) in pyridine (90 ml) was added the diol (14; R = Pr^i) (10 g) dissolved in pyridine (100 ml). After 24 h the mixture was poured into water and extracted with light petroleum–ether (1 : 1). The combined extracts were filtered through Kiesulguhr and evaporated. The crystalline solid (8·29 g, 84%), m.p. 130—131°, was recrystallised to give 3-*hydroxy*-3-*isopropyl*-3(5 ⟶ 6β H)-*abeo*-A-*norcholest*-7-*en*-5-*one* (12; R = Pr^i) as the dimorphous product, m.p. 134° (from di-isopropyl ether or ethanol) and 144° (from light petroleum), $[\alpha]_D$ +120° (Found: C, 81·65; H, 11·25. $C_{29}H_{48}O_2$ requires C, 81·25; H, 11·4%).

Attempted oxidation with ether chromium trioxide in acetone or aluminium isopropoxide–cyclohexanone in toluene returned starting material (28 and 72% respectively).

Dehydration of the ketol (12; R = Pr^i) (500 mg) in pure pyridine (25 ml) with phosphorus oxychloride (1 ml) for 3 h at 90° and work-up gave a mixture of *compounds* (21), $\lambda_{max.}$ (ethanol) 296 nm (ε 300), $[\alpha]_D$ +260° (Found: C, 84·25; H, 11·45. $C_{29}H_{46}O$ requires C, 84·8; H, 11·3%).

3-*Hydroxy*-3-*isopropyl*-3(5 ⟶ 6β H)abeo-A-*norcholestan*-5-*ol* (22).—A stock solution of isopropylmagnesium bromide {from isopropyl bromide (10 ml), magnesium (5 g), and anhydrous ether (200 ml)} was standardised and 1·1 equivalents were added to a stirred solution of the lactone (1) (5 g) in ether (150 ml) under nitrogen during 15 min. After 12 h work-up as for (9; R = Me) gave a product which was dissolved in benzene and chromatographed on alumina (6% H_2O). The benzene–ether eluates gave, as a first fraction (*ca.* 100 mg), a compound m.p. 156—157° (from di-isopropyl ether) followed by a mixture (2·42 g, 44%) of compounds (15) and (22). Repeated crystallisation gave *pure* (22), m.p. 212—214° (from di-isopropyl ether), $[\alpha]_D$ +12° (Found: C, 80·5; H, 12·1. $C_{29}H_{52}O_2$ requires C, 80·5; H, 12·1%).

3-*Hydroxy*-3-*isopropyl*-3(5 ⟶ 6β H)abeo-A-*norcholestan*-5-*one* (15).—(*a*) The mixture of compounds (15) and (22), m.p. 170—172°, (2 g) in acetone (300 ml) was treated with Jones' chromic acid reagent [28] (1·5 equiv.). Work-up gave *compound* (15) (1·66 g, 83%), m.p. 158·5—159·5° (from di-isopropyl ether), $[\alpha]_D$ +18° (Found: C, 81·25; H, 11·6. $C_{29}H_{50}O_2$ requires C, 80·85; H, 11·7%).

(*b*) Mesityl bromide (10 ml) in ether (100 ml) and tetrahydrofuran (10 ml) was treated with magnesium (2·5 g)

[28] A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 1953, 2548.

under nitrogen. After completion of the reaction, the mixture was filtered through glass wool and a portion was standardised. This solution (6 ml., 1·1 mol) was added during 15 min to 3-isopropyl-3,5-seco-A-norcholestane-3,5-dione (16) (1 g) (see below) in ether (25 ml). After 4 h work-up gave (260 mg, 26%) 3-hydroxy-3-isopropyl-3(5 → 6βH)-*abeo*-A-norcholestan-5-one (15) identical with that obtained in (*a*) above.

3-*Isopropylidene*-3(5 → 6βH)abeo-A-*norcholestan*-5-*one* (20).—The ketol (15) (500 mg) in pure dry pyridine (20 ml) was treated with freshly distilled phosphorus oxychloride (0·9 ml) and the solution was heated under a condenser (with rigorous exclusion of moisture) at 90° for 3 h. The mixture was cooled and benzene–di-isopropyl ether (1 : 1) was added; it was then washed with dilute hydrochloric acid, dilute potassium hydroxide solution, and then water; it was dried and evaporation gave (310 mg, 65%) *compound* (20), m.p. 150—151° (from di-isopropyl ether), $\lambda_{max.}$ (ethanol) 205 (ε 6300), 220sh and 296 nm (ε 360); $[\alpha]_D$ +43°; $\nu_{max.}$ (CCl_4) 1717, 1297, 1161, and 1143 cm^{-1}; τ 9·37 (13-Me), 9·04 (10-Me), 9·14 (d, *J* 6 Hz) (26- and 27-Me), 8·32 (coincident isopropylidene Me), and 6·37 (complex d, *J* 11·5 Hz, 6-H) (Found: C, 85·2; H, 11·95. $C_{29}H_{48}O$ requires C, 84·4; H, 11·7%).

3-*Isopropyl*-A-*norcholest*-3(5)-*ene* (18).—4,4-Dimethylcholest-5-en-3β-ol [18] was converted into 4,4-dimethyl-5α-cholestan-3β-ol and thence to 3-isopropylidine-A-nor-5α-cholestane by the published methods.[19,20] A solution of 3-isopropylidene-A-nor-5α-cholestane (10 g) in ethanol (1·5 l) and carbon tetrachloride (100 ml) was heated under reflux with concentrated hydrochloric acid (60 ml) for 13 hours; the solution was then concentrated to 1 l. and cooled with occasional shaking. The crystalline 3-*isopropyl*-A-*norcholest*-3(5)-*ene* (18) (8·11 g, 81%), m.p. 54—55° was recrystallised from ethyl acetate, m.p. 55—56°, $[\alpha]_D$ +58°; $\nu_{max.}$ (KBr) 1664w and 1027 cm^{-1}; τ 9·31, 9·17, 9·13, 9·07, 9·02, and 8·97 (Me) (Found: C, 87·3; H, 12·5. $C_{29}H_{50}$ requires C, 87·35; H, 12·65%).

3-*Isopropyl*-3,5-*seco*-A-*norcholestane*-3,5-*dione* (16). (*a*) Ozone was passed into a solution of 3-isopropyl-A-norcholest-3(5)-ene (2·0 g) in dichloromethane (180 ml) and methanol (40 ml) at −78° until a permanent blue colour developed. After being warmed to 0° the mixture was stirred for 1 h with acetic acid (40 ml) and zinc powder (10 g). The mixture was filtered, washed successively with water, aqueous sodium hydrogen carbonate and water and finally dried and evaporated. The oil was chromatographed in benzene on alumina (3% H_2O). The light petroleum fractions furnished 3-*isopropyl*-A-*norcholestan*-3,5-*epoxide* (19), m.p. 120° (from chloroform–methanol), $[\alpha]_D$ +45°; $\nu_{max.}$ (KBr) 1200, 1021, 962, 918, and 874 cm^{-1}; τ 9·32, 9·16, 9·12, 9·02, 8·92, 8·81, and 8·74 (Me) (Found: C, 83·6; H, 12·15. $C_{29}H_{50}O$ requires C, 84·0; H, 12·15%).

The benzene fractions furnished 3-*isopropyl*-3,5-*seco*-A-*norcholestane*-3,5-*dione* (16) (1·65 g, 77%) as an oil $[\alpha]_D$ +47°; $\nu_{max.}$ (CCl_4) 1706, 1447, 1430, 1096, and 953 cm^{-1}; τ 9·25, 9·18, 9·08, 8·97, 8·87, and 8·84 (Me) (Found: C, 80·5; H, 11·4. $C_{29}H_{50}O_2$ requires C, 80·85; H, 11·7%). The *bis*-2,4-*dinitrophenylhydrazone* had m.p. 190—191°, $\lambda_{max.}$ ($CHCl_3$) 364 nm (ε 43,500) (Found: C, 61·95; H, 7·35; N, 14·35. $C_{41}H_{58}N_8O_8$ requires C, 62·25; H, 7·4; N, 14·15%).

(*b*) The ozonisation of 3-isopropyl-A-norcholest-3(5)-ene was conducted as in (*a*) above except that after being warmed to 0° the solution was stirred with water (80 ml) containing hydrogen peroxide (100 volume; 2 ml). The organic phase was separated, dried, and evaporated and the product was chromatographed on silica gel and then on alumina. 3-*Isopropyl*-A-*norcholest*-3(5)*ene ozonide* had m.p. 79—80°, $[\alpha]_D$ +79°; $\nu_{max.}$ (film) 1442, 1294, and band progressions from 1122—1080 and from 1030—907 cm^{-1} (Found: C, 77·75; H, 11·3. $C_{29}H_{50}O_3$ requires C, 77·95; H, 11·3%). Reduction of this ozonide in chloroform–acetic acid gave quantitatively the diketone (16).

(*c*) 3-Hydroxy-3-isopropyl-3(5 → 6βH)*abeo*-A-norcholestane (15) (1 g) was heated with a solution of sodium (2·5 g) in absolute methanol (100 ml) for 6 h at 90° under nitrogen. Work-up gave almost quantitatively (940 mg) 3-isopropyl-3,5-seco-A-norcholestane-3,5-dione (16).

(*d*) Compound (15) (1 g) in light petroleum–benzene was applied to alumina (6% H_2O) (35 g) and after 10 hours The column was eluted with light petroleum–benzene. Evaporation of the eluates left pure diketone (600 mg) (16).

Cyclisation of Compounds (15) *and* (16).—(*a*) Benzene (50 ml) and toluene-*p*-sulphonic acid (500 mg) were heated under reflux under a water separator for 30 min, 3-hydroxy-3-isopropyl-3(5 → 6βH)*abeo*-A-norcholestan-5-one (15) (600 mg) was then added and heating was continued for 3 h. Work-up gave an oil which by t.l.c. was shown to consist mainly of the ketone (16) and material of high R_F. Chromatography of the oil on alumina (6% H_2O) (30 g) gave in the first light petroleum fractions a hydrocarbon (q.v.). The later light petroleum fractions gave a *crystalline solid* (47 mg), m.p. 125—126° (from light petroleum–methanol) (Found: C, 84·2; H, 11·55. $C_{29}H_{48}O$ requires C, 84·4; H, 11·7%) not further investigated.

The light petroleum–benzene fractions (up to 20% benzene) gave a product which was further chromatographed by p.l.c. with benzene as developer and 50% sulphuric acid as spray detection reagent. The upper band gave a *compound* (9·7 mg), m.p. 80·5—81·5° (from aqueous ethanol) (Found: C, 84·65; H, 11·5. $C_{29}H_{48}O$ requires C, 84·4; H, 11·7%). The lower band furnished pure 4,4-dimethylcholest-5-en-3-one (10·1 mg), m.p. 174—175° (from ethanol), identical with an authentic specimen.[18] In t.l.c. the compound gives a transient pink colour when sprayed with 50% sulphuric acid and heated.

The benzene and benzene–ether fractions gave the diketone (16).

(*b*) The diketone (16) was treated as in (*a*) above. 4,4-Dimethylcholest-5-en-3-one (9·3 mg) and the compound m.p. 80·5—81·5° (3·5 mg) were obtained.

1,3,4-*Trimethyl*-19-*norcholesta*-1,3,5(10)-*triene* (25). The diketone (16) (1·5 g) was heated under reflux with toluene-*p*-sulphonic acid (500 mg) in benzene (50 ml) under a water separator for 48 h. Work-up gave an oil which was chromatographed in light petroleum on alumina (6% H_2O). The oil (1·13 g) had $\lambda_{max.}$ (cyclohexane) 270 nm ($E^{1\%}_{1\,cm.}$ 19), 278 nm ($E^{1\%}_{1\,cm}$ 17), τ (CCl_4) 7·94, 7·83, 7·78, 7·60 (aromatic Me), and 3·35br (ArH), and a portion was further purified by p.l.c. (silica gel–5% $AgNO_3$) and gave 1,3,4-trimethyl-19-norcholest-1,3,5(10)-triene (25) as an oil,[24] $\nu_{max.}$ (CCl_4) 1603w, 1570, 1523, 1252, and 867 cm^{-1}; τ (CCl_4) 7·96, 7·84 and 7·78 (ArMe individual assignments unknown), and 3·31 (s, 2-H) (Found: C, 88·25; H, 11·65. Calc. for $C_{29}H_{46}$: C, 88·25; H, 11·75%).

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