Steric Factors in the Hydrogenolysis of Some Steroidal Allylic Alcohols by Mixed Hydrides

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The allylic steroidal alcohols 3β,7β- and 3β,7α-dihydroxycholest-5-ene [(5) and (7)], the corresponding 7-deuterio-compounds [(6) and (8)], and 3α- and 3β-hydroxycholest-4-ene [(12) and (13)] have been hydrogenolysed with dichloroaluminium deuteride or hydride and the α : β ratio of allylic deuterium has been determined for each product. The results are intelligible in terms of hydride capture *via* reactant-like transition states resembling the initially formed allylic carbonium ions.

In the course of other work it became necessary to synthesise cholesterol stereoselectively deuteriated in the 7α- or 7β-position. This had been accomplished previously by Corey and Gregoriou [1] by a sequence having as its key step stereoselective deuteriation at C-7 of 3β-acetoxycholest-6-en-6-ol or protonation of the corresponding 7-deuterio-compound. It seemed to us that deuteriolysis of 7β-hydroxycholesterol or hydrogenolysis of the corresponding 7α-deuterio-compound with the mixed lithium aluminium deuteride (hydride)–aluminium chloride reagent [2,3] might provide a simpler route.

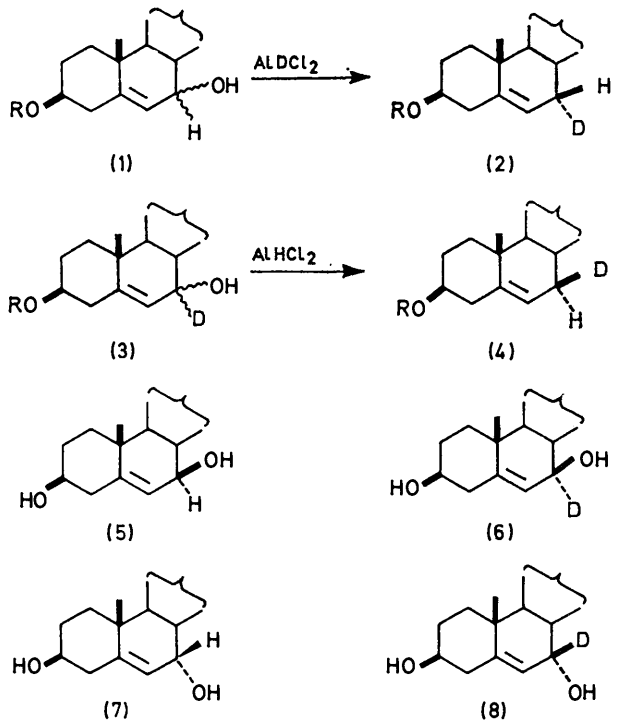
The mechanism of reduction by mixed hydride–aluminium halide reagents of a variety of functional groups has been studied extensively.[2-5] Of particular relevance is the conclusion that hydrogenolysis of allylic alcohols proceeds *via* allylic carbonium ions.[1,5c,6]

[1] E. J. Corey and G. A. Gregoriou, *J. Amer. Chem. Soc.*, 1959, **81**, 3127.
[2] E. L. Eliel, *Rec. Chem. Progr.*, 1961, **22**, 129.
[3] (*a*) E. C. Ashby and J. Prather, *J. Amer. Chem. Soc.*, 1966, **88**, 729; (*b*) E. C. Ashby and B. Cooke, *ibid.*, 1968, **90**, 1625.
[4] M. N. Rerick and E. L. Eliel, *J. Amer. Chem. Soc.*, 1962, **84**, 2356.
[5] (*a*) J. H. Brewster and H. O. Bayer, *J. Org. Chem.*, 1964, **29**, 105; (*b*) J. H. Brewster, H. O. Bayer, and S. F. Osman, *ibid.*, p. 110; (*c*) J. H. Brewster and H. O. Bayer, *ibid.*, p. 116.
[6] J. Broome, B. R. Brown, A. Roberts, and A. M. S. White, *J. Chem. Soc.*, 1960, 1406.

There was at the time no indication in the literature as to the stereochemical outcome of such allylic hydrogenolyses, but it seemed likely that a cholest-5-en-7-yl cation would capture hydride predominantly from the α-face. On this assumption, stereoselective introduction of deuterium into the 7α- or 7β-position of cholesterol proceeding from either 7α- or 7β-hydroxycholesterol becomes possible, as illustrated in the conversions (1) ⟶ (2) and (3) ⟶ (4).

We first describe syntheses of the four 7-hydroxycholesterols (5)—(8) and then the method used to analyse the products formed from each by reduction with the mixed hydride reagent dichloroaluminium hydride or deuteride.

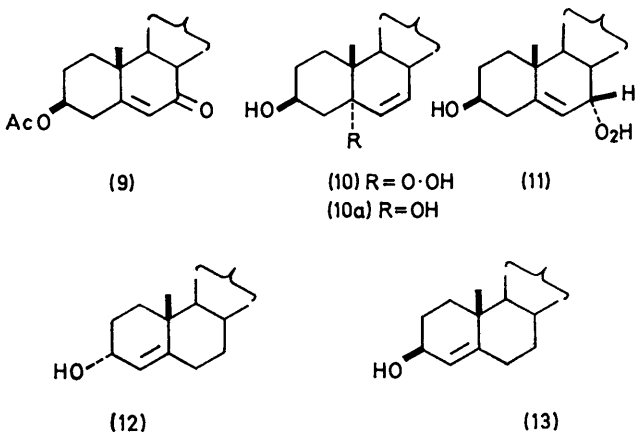
7-Oxocholesteryl acetate (9) was obtained from cholesteryl acetate by treatment with anhydrous sodium chromate in acetic acid–acetic anhydride. Reduction of the enone (9) with lithium aluminium hydride in ether at −20° afforded 7β-hydroxycholesterol (5) and 7α-hydroxycholesterol (7) (9 : 1). Reduction with lithium aluminium deuteride similarly afforded the 7-deuterio-compounds (6) and (8). 7α-Hydroxycholesterol (7) was prepared more efficiently by a three-stage sequence comprising (i) photosensitised oxidation



of cholesterol,[7a] (ii) rearrangement of the 5α-hydroperoxy-3β-hydroxycholest-6-ene (10) so produced to 7α-hydroperoxycholesterol (11),[7a] and (iii) reduction with sodium borohydride. 7,7-Dideuterio-cholesterol similarly furnished 7β-deuterio-7α-hydroxycholesterol (8).

[7] (*a*) G. O. Schenk, K. Gollnick, and O. A. Neumuller, *Annalen*, 1957, **603**, 46; (*b*) G. O. Schenk, O. A. Neumuller, and W. Eisfield, *ibid.*, 1958, **618**, 202; B. Lythgoe and S. Trippett, *J. Chem. Soc.*, 1959, 471.

Hydrogenolysis or deuteriolysis of the allylic alcohols (5)—(8) to the 7-deuteriocholesterols was effected by a



standard procedure described in the Experimental section, in which the effective reducing agent was dichloroaluminium hydride (deuteride) prepared from lithium aluminium hydride (deuteride) and aluminium chloride (1 : 4). To determine the proportions of deuterium label in the 7α- and 7β-positions of the product from each hydrogenolysis, the cholesterol was photo-oxygenated and the deuterium content of the resulting 3β,5α-dihydroxycholest-6-ene was determined by mass spectrometry. Since the photo-oxygenation of cholesterol has been shown [8] to remove specifically the 7α-hydrogen atom, this provides a direct measure of the deuterium content at the 7α- and 7β-positions. The results (Table 1) demonstrate a high degree of

TABLE 1

Stereoselectivity in the hydrogenolysis by dichloroaluminium hydride of the 7α- and 7β-hydroxycholesterols

Reactant	Reducing agent	Product	% Allylic D α	% Allylic D β	Ref.
(5)	$AlDCl_2$	Cholesterol	97	3	This paper
(6)	$AlHCl_2$		18	82	
(7)	$AlDCl_2$		91	9	
(8)	$AlHCl_2$		12	88	
(9)	$LiAlH_4$	(5) + (7)	22	78	
			(7)	(5)	
(12)	$AlDCl_2$	Cholest-4-ene	84	12	This paper
(12)	$AlDCl_2$		85	15	11
(12)	AlD_2Cl		85	15	11
(13)	$AlDCl_2$		48	49	This paper
(13)	$AlDCl_2$		35	65	11
(13)	AlD_2Cl		65	35	11
Cholestenone	$LiAlH_4$	(12) + (13)	11 (12)	89 (13)	This paper

selectivity in the predicted sense for the hydrogenolysis by dichloroaluminium hydride of the 7α- and 7β-hydroxycholesterols.

We then became interested in the hydrogenolysis of allylic alcohols that should generate allylic carbonium ions equally accessible to hydride attack from either direction, and chose the cholest-4-en-3α- and -3β-ols

[8] A. Nickon and J. F. Bagli, *J. Amer. Chem. Soc.*, 1961, **83**, 1498.

(12) and (13) for study. An additional attraction here was the much greater conformational mobility of ring A which might disclose stereoelectronic preferences in the reaction not observable with allylic carbonium ions confined within the rigid geometry of ring B.

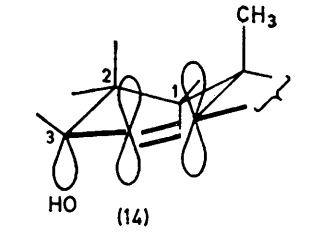
The 3α- and 3β-hydroxycholest-4-enes were readily prepared by reduction with lithium aluminium hydride of cholest-4-en-3-one (product ratio 11 : 89, estimated by n.m.r.). They could not be readily separated on a preparative scale by layer chromatography but the 3β-acetate was readily obtained by crystallisation and the epimeric α-acetate was recovered from the mother liquors by preparative layer chromatography. Deuteriolysis of the alcohols was effected as previously with dichloroaluminium deuteride; the deuteriated alcohols were not hydrogenolysed in this case.

Analysis of the deuterium distribution between the 3α- and 3β-positions of the cholest-4-enes formed presented a more difficult problem since photo-oxygenation does not, in this case, remove one allylic (C-3) hydrogen atom stereospecifically,[9] presumably because of the conformational mobility of ring A. A less direct procedure had therefore to be devised. Each cholest-4-ene was hydroborated [10] and the resulting 4α-hydroxy-5α- and 4β-hydroxy-5β-cholestanes were separated chromatographically. The 3α-H : 3β-H ratio was then determined by integration of the appropriate signals in the n.m.r. spectrum of a solution containing the shift reagent $Eu(fod)_3$; * the 5β- and 6α-proton signals were used as internal standards. The results are shown in Table 1.

After completion of our own work, the results of analogous experiments with 3α- and 3β-hydroxycholest-4-ene were reported.[11] Paradisi and Romeo used a different analytical procedure and it is not evident whether their conditions of hydrogenolysis were strictly comparable with ours. Agreement between the two sets of results is much better for the 3α-alcohol, where the ratio of products formed should depend much less critically on the reagent composition (see Paradisi and Romeo's results with mono- and dichloroaluminium deuteride) than for the 3β-alcohol (see Discussion section).

DISCUSSION

The most surprising result from our experiments is that the proportion of α- to β-hydride capture at C-3 depends markedly on whether 3α- or 3β-hydroxycholest-4-ene is the alcohol undergoing hydrogenolysis. This certainly rules out intermediacy of the *same* allylic carbonium ion in the two cases. However, it does not rule out the intermediacy of two conformationally distinct allylic carbonium ions, separated by a sufficiently large conformational barrier and formed stereospecifically from the two reactants. Goering and Josephson [12] have rationalised the solvolytic behaviour of *cis*- and *trans*-5-methylcyclohex-2-enols by assuming that fission of the allylic C–O bond occurs most readily when it is in a plane perpendicular to that of the olefinic double bond. If we accept a similar requirement for hydrogenolysis mediated by dichloroaluminium hydride of the isomeric 3-hydroxycholest-4-enes, then the 3α-alcohol (12) will lead directly to the allylic carbonium ion (15),† whose half-chair conformation is close to that of the reactant alcohol ground state (14) while the 3β-alcohol (13) will react *via* a half-boat conformation (16) to afford the related carbonium ion (17).†



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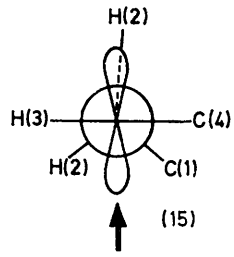

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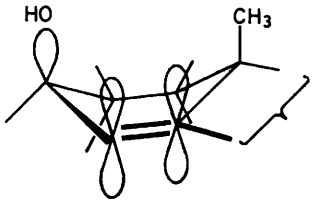

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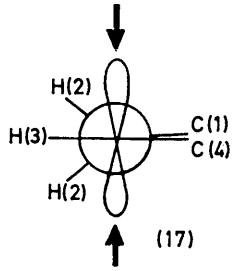

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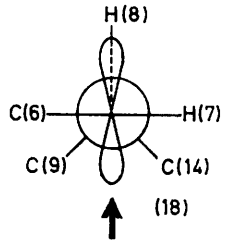

(18)

Goering [12] has pointed out that the barrier separating such a pair of cyclohexenyl cations may be unexpectedly high (possibly approaching that for the chair–chair interconversion in cyclohexane), so that it may not be unreasonable to consider hydride capture in the two cases *via* transition states resembling the ions (15) and (17).‡ If torsional strain between the incoming hydride and the neighbouring (C-2) C–H bonds is important,[13] then hydride attack on (15) from the α-side

* $Eu(dpm)_3$ did not separate the critical signals.

† For clarity only the Newman projection along the C(3)–C(2) bond is shown for the carbonium ions (15) and (17).

‡ We thank Professor J. K. Sutherland for alerting us to this possibility.

[9] A. Nickon and W. L. Mendelson, *Canad. J. Chem.*, 1965, **43**, 1419.

[10] J. R. Bull, E. R. H. Jones, and G. D. Meakins, *J. Chem. Soc.*, 1965, 2601.

[11] M. P. Paradisi and A. Romeo, *J.C.S. Perkin I*, 1972, 2010.

[12] H. L. Goering and R. R. Josephson, *J. Amer. Chem. Soc.*, 1962, **84**, 2779.

[13] M. Cherest, H. Felkin, and N. Prudent, *Tetrahedron Letters*, 1968, 2199; M. Cherest and H. Felkin, *ibid.*, p. 2205.

must be vastly preferred over β-attack, as is observed. On this basis, there should be no preference in the case of the carbonium ion (17) formed from the 3β-alcohol, since the two (C-2) C–H bonds are equally disposed with regard to the vacant *p*-orbital at C-3. Indeed, the two products from α- and β-hydride attack are in this case formed in comparable amounts.

Because of its fusion to rings A and C, the 5-en-7-yl cation (18) has little conformational choice. Regardless of whether it is generated from the 7α- or the 7β-alcohol, hydride capture will take place predominantly from the α-face, thereby escaping the torsional strain with the C(8)–H bond that would arise during β-attack.

It is interesting that the proportions of allylic alcohols from hydride reduction (see Table) of the 4-en-3-one and 5-en-7-one systems closely mirror the products of hydride capture by the corresponding allylic carbonium ions. Such a parallel is anticipated on the basis of torsional strain in reactant-like transition states [13] as developed above.

EXPERIMENTAL

The following instruments were used: for i.r. spectra Perkin-Elmer 257 and 225 and Unicam SP 100 (solutions in CCl_4); for n.m.r. spectra Varian T60 and HA100 (solutions in $CDCl_3$); for mass spectra A.E.I. MS12, MS902, and LKB 9000 (g.l.c.-linked); for g.l.c. Pye-Argon and Perkin-Elmer F11. T.l.c. was performed on Merck Kieselgel HF 254 [0·25 mm (analytical) and 1·00 mm (preparative)].

Preparation of 7β- *and* 7α-*Hydroxycholesterols* [(5) *and* (7)] *and the* 7-*Deuterio-compounds* [(6) *and* (8)].—7-*Oxocholesteryl Acetate* (9). Anhydrous sodium chromate [14] (7·3 g, 45 mmol) was added under nitrogen at 60° to cholesteryl acetate (9 g, 21 mmol). The mixture was stirred for 20 h in acetic acid (70 ml) and acetic anhydride (30 ml), cooled, and diluted with ice–water; the precipitate afforded 7-oxocholesteryl acetate (9) (7·1 g, 76%), m.p. 159—160° (from hot acetic acid) (lit.,[15] 158—159°).

7β- *and* 7α-*Hydroxycholesterol by reduction of* 7-*oxocholesteryl acetate.* Reduction with lithium aluminium hydride at 0° under the usual conditions afforded a mixture of the 3β,7α- and the 3β,7β-diol (22 : 78, estimated by integration of C*H*OH–CH=C n.m.r. signals at 100 MHz) separable by preparative t.l.c. (ethyl acetate–light petroleum, 1 : 1). 7β-Hydroxycholesterol (5) had m.p. 172—174° (lit.,[16,17] 172—176°), $\nu_{max.}$ 3615 and 1040 cm^{-1}; δ 5·26br (1H, s), 3·80 (1H, d, *J* 6 Hz), and 3·60 (1H, m). 7α-Hydroxycholesterol (7) had m.p. 181—183° (lit.,[16,17] 183—184°), $\nu_{max.}$ 3615, 1050 and 935 cm^{-1}; δ 5·58 (1H, d, *J* 6 Hz), 3·84 (1H, d, *J* 6 Hz), and 3·56 (1H, m). From a reaction at −20° the proportion of 7β- to 7α-hydroxycholesterol was 9 : 1.

Reduction of the oxo-acetate (9) with lithium aluminium deuteride at −20° afforded as major product 7α-deuterio-7β-hydroxycholesterol (6), $\nu_{max.}$ 3615, 2120, and 1040 cm^{-1}; δ 5·28 (1H, s) and 3·60 (2H, m); isotope ratios for *m/e* 402/403/404/405, 28·5 : 100 : 30·9 : 7 (Calc. for $C_{27}H_{45}DO_2$: 403/404/405, 100 : 29·7 : 2).

7α-*Hydroxycholesterol* via *photo-oxygenation of cholesterol.* Photo-oxygenation of cholesterol [7] and reduction with borohydride of the resulting hydroperoxide (10) afforded cholest-6-ene-3β,5α-diol (10a) (75%), m.p. 180—181° (lit.,[7] 181°), $\nu_{max.}$ 3622, 3015, 1635, 1037, 1018, 950, and 862 cm^{-1}; δ 5·60 (2H, s) and 4·10 (1H, m); M^+ 402; isotopic ratios for *m/e* 401/402/403/404, 15·5 : 100 : 31 : 8 and for *m/e* 384/385/386, 100 : 32 : 6·5 [used in calculating the deuterium contents of samples of cholest-6-ene-3β,5α-diols obtained from the deuteriated cholesterols (A)—(D) by the analytical procedure described below].

The hydroperoxide (10), dissolved in chloroform and stirred at 20° for 24 h, rearranged to the isomer (11), which was reduced directly with borohydride to afford 7α-hydroxycholesterol (7), m.p. (from methanol) 182—183° [45% from the hydroperoxide (10)].

Photo-oxygenation of 7,7-dideuteriocholesterol [obtained from the enone acetate (9) with dichloroaluminium deuteride (6 mol. equiv.)], rearrangement of the tertiary hydroperoxide, and reduction with borohydride afforded 7β-deuterio-7α-hydroxycholesterol (8), $\nu_{max.}$ 3620, 2130, 1655, 1115, 1052, and 1040 cm^{-1}; δ 5·60 (1H, s) and 3·55 (1H, m); M^+ 403.

Hydrogenolysis of the 7-*Hydroxycholesterols* (5)—(8); *Standard Procedure.*—To anhydrous aluminium chloride (8 mmol) in dry ether (40 ml) at 0° under nitrogen was added lithium aluminium hydride (or deuteride) (2 mmol) in dry ether, and the mixture was stirred for 10 min. The allylic alcohol (1 mmol) in ether was added, stirring was continued for 15 min more, and the reaction was quenched by dropwise addition of water. The resulting cholesterol was isolated as usual in 75—90% yields.

Hydrogenolysis or deuteriolysis by the above procedure afforded four specimens of 7-deuteriocholesterol as follows. Deuteriolysis of 7β-hydroxycholesterol (5) gave the deuteriocholesterol (A), $\nu_{max.}$ 3625, 3013, 2120, 2098, 1048, and 948 cm^{-1}; δ 5·35 (1H, d, *J* 5 Hz) and 3·52 (1H, m); M^+ 387; isotopic ratios for *m/e* 386/387/388/389, 7 : 100 : 31 : 4 (Calc. for $C_{27}H_{45}DO$: 387/388/389, 100 : 29·7 : 2).

Hydrogenolysis of 7α-deuterio-7β-hydroxycholesterol (6) gave the deuteriocholesterol (B), $\nu_{max.}$ 3621, 3027, 2156, 2144, 1047, and 949 cm^{-1}; δ 5·37 (1H, s) and 3·50 (1H, m); M^+ 387; isotopic ratios for *m/e* 386/387/388/389, 8 : 100 : 30 : 4.

Deuteriolysis of 7α-hydroxycholesterol (7) gave the deuteriocholesterol (C), $\nu_{max.}$ 3622, 2110, 2090, 1660, 1110, 1045, 1020, and 945 cm^{-1}; δ 5·37 (1H, d, *J* 6 Hz) and 3·55 (1H, m); M^+ 387; isotopic ratios for *m/e* 387/388/389, 100 : 29 : 5.

Hydrogenolysis of 7β-deuterio-7α-hydroxycholesterol (8) gave the deuteriocholesterol (D), $\nu_{max.}$ 3622, 2150, 2137, 1660, 1110, 1045, 1035, and 943 cm^{-1}; δ 5·37 (1H, s) and 3·55 (1H, m); M^+ 387; isotopic ratios for *m/e* 387/388/389, 100 : 30·5 : 5.

Determination of 7α- *and* 7β-*Deuterium Content in the Deuteriocholesterols* (A)—(D).—Each specimen of deuteriocholesterol was photo-oxygenated as described for the preparation of 7α-hydroxycholesterol *via* photo-oxygenation of cholesterol. The cholest-6-ene-3β,5α-diol was obtained pure and the residual deuterium (at C-7 from 7β-D) was estimated by mass spectrometry. Thus were obtained the following specimens of cholest-6-ene-3β,5α-diol.

[14] C. W. Marshall, R. E. Ray, I. Loos, and B. Riegel, *J. Amer. Chem. Soc.*, 1957, **79**, 6308.

[15] L. F. Fieser, W.-Y. Huang, and B. K. Bhattacharyya, *J. Org. Chem.*, 1957, **22**, 1380.

[16] L. F. Fieser, J. E. Herz, M. W. Klohs, M. A. Romero, and T. Utne, *J. Amer. Chem. Soc.*, 1952, **74**, 3309.

[17] H. Danielson, *Acta Chem. Scand.*, 1960, **14**, 846.

From the deuteriocholesterol (A): $\nu_{max.}$ 3622, 3015, 1635, 1307, 1019, 949, and 862 cm^{-1}; δ 5·60 (2H, s) and 4·10 (1H, m); isotope ratios for *m/e* 402/403/404, 100 : 52 : 13·5. The unlabelled sample (see above) had ratios for *m/e* 401/402/403/404, 15·5 : 100 : 31 : 8. From this.

$$\frac{D_0}{D_1} = \frac{100 - (15{\cdot}5 \times 21/100)}{52 - 31} = \frac{96{\cdot}5}{21}$$

Hence D_1 content = 17·5% corresponding to 17·5% β-*D* and 82·5% α-*D* in the deuteriocholesterol (1). Similar photo-oxygenation and mass spectrometric analysis gave the following results for the other deuteriocholesterols: (B): 97·0% β-D, 3·0% α-D; (C): 9·0% β-D, 91% α-D; (D): 88·0% β-D, 12% α-D.

Reduction of Cholest-4-en-3-one with Lithium Aluminium Hydride.—Reduction under standard conditions and separation by preparative t.l.c. (ethyl acetate–light petroleum, 1 : 4) afforded cholest-4-en-3β-ol, m.p. 131—133° (lit.,[18] 130—132°), δ 5·24 (1H, d, *J* 1 Hz) and 4·12 (1H, m); and cholest-4-en-3α-ol, m.p. 82—84° (lit.,[18] 83—84°), δ 5·45 (1H, d, *J* 5 Hz) and 4·06 (1H, m). Relative proportions of 3β- to 3α-ol in the crude product were 89 : 11 (by integration of n.m.r. signals at δ 5·45 and 5·24). On a preparative scale, separation of the two alcohols was effected by crystallisation of the acetates [19] and regeneration of alcohols by hydride reduction.

Deuteriolysis of Cholest-4-en-3β- and 3α-ol.—The 3β-compound with dichloroaluminium deuteride under conditions as previously afforded the deuteriocholest-4-ene (E), $\nu_{max.}$ 2125, 1658, 1440, 1372, and 933 cm^{-1}; δ 5·28 (1H, d, partly resolved); M^+ 371. The 3α-compound afforded the deuteriocholest-4-ene (F), $\nu_{max.}$ 2120, 1655, 1465, 1440, 1372, and 933 cm^{-1}; δ 5·29 (1H, d, *J* 5 Hz); M^+ 371.

Hydroboration of Cholest-4-ene.—Hydroboration [10] of cholest-4-ene (1·5 g, 4 mmol) gave an alcohol mixture (1·3 g) which on repeated preparative layer chromatography (ethyl acetate–light petroleum 3 : 17) afforded 5β-cholestan-4β-ol and 5α-cholestan-4α-ol,[20] each identical with a specimen prepared for comparison from the corresponding ketone. 5β-Cholestan-4β-ol had $\nu_{max.}$ 3628, 1050, 1030, 1020, 1008, and 920 cm^{-1}; δ 3·94br (1H, s, *W* 20 Hz) and 0·97, 0·91, 0·81, and 0·62 (methyls); M^+ 388. 5α-Cholestan-4α-ol had m.p. 185—187° (lit.,[20] 186—187°), $\nu_{max.}$ 3640, 1065, 1035, and 945 cm^{-1}; δ 3·62br (1H, *s*, *W* 20 Hz) and 0·94, 0·82, and 0·64 (methyls); M^+ 388.

Hydroboration as above of the deuteriocholest-4-enes (E) and (F) afforded the corresponding 3-deuteriocholestan-4-ols.

N.m.r. Analysis of the Deuterio-alcohols obtained from Hydroboration of the Deuteriocholest-4-enes (E) *and* (F).—The 100 MHz n.m.r. spectra of the separated alcohols from each hydroboration were recorded in $CDCl_3$ solution with sufficient (as determined with the unlabelled alcohols) added $Eu(fod)_3$ shift reagent to separate the signals from 3α- and 3β-protons. Chemical shifts for the relevant protons and the basis for their assignment are shown in Tables 2 and 3. Deuterium content was estimated in each case by repeated integration, calibrated against internal standards (5β- and 6α-H). It was thus shown that the cholest-4-ene (E) from cholest-4-en-3β-ol had 3α-D 48%, 3β-D 49% (50 and 46; 46 and 52% for the 5α-cholestan-4α-ol and the 5β-cholestan-4β-ol, respectively); and the cholest-4-ene (F) from cholest-4-en-3α-ol had 3α-D 84% and 3β-D 12% (81 and 15; 87 and 9% for the corresponding products).

TABLE 2

Assignments for the ^1H n.m.r. spectrum at 100 MHz of 5β-cholestan-4β-ol with $Eu(fod)_3$ (0·45 equiv.)

Peak	Position *	Multiplicity	Effect of decoupling at peak	Assignment
1	15·18	br, s	5 becomes s, 3 and 4 sharpen	4α
2	9·39	d, *J* 14 Hz	6 becomes d, *J* 14 Hz	6α
3	9·12	d, *J* 12 Hz	1 sharpens	3α
4	8·68	t, *J* 11 Hz	1 sharpens	3β
5	8·06	d, *J* 9 Hz	1 sharpens	5β
6	4·86	t, *J* 14 Hz	2 becomes s	6β
7	4·30	q	8 becomes s	7α?
8	2·90	d, *J* 10 Hz		7β?
9	2·66	s (3H)		10-Me

TABLE 3

Assignments for the ^1H n.m.r. spectrum at 100 MHz of 5α-cholestan-4α-ol with $Eu(fod)_3$ (0·8 equiv.)

Peak	Position *	Multiplicity	Effect of decoupling at peak	Assignment
1	>20·00		5 becomes d, *J* 10 Hz 3 and 4 sharpen	4β
2	13·52	d	6 becomes t 5 sharpens	6α
3	12·62	br, m		3α
4	11·98	d		3β
5	11·74	t	6 becomes t	5α
6	6·84	q		6β

* In p.p.m. downfield from Me_4Si.

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