

516. *Steroids and Walden Inversion. Part LI.* The Solvolysis of 4,4-Dimethylcholest-5-en-3 α -yl Toluene-p-sulphonate.*

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Solvolysis of 4,4-dimethylcholest-5-en-3 α -yl toluene-*p*-sulphonate gives the corresponding 3 α -alcohol (10%) [or acetate (5%)], 3 β ,4 β -dimethylcholest-5-en-4 α -ol (5%), and 3,4-dimethylcholesta-3,5-diene (85%). The reaction is not synartetically accelerated, and is regarded as proceeding through a classical carbonium ion, which rapidly gives a non-classical bridged cation of greater thermodynamic stability.

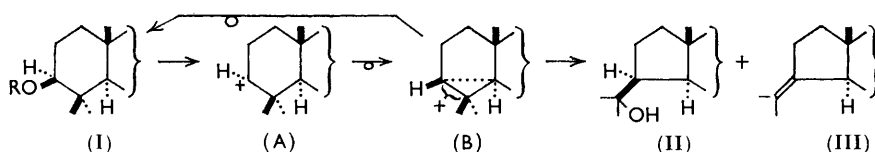
Some reactions of epimeric 4,4-dimethylcholest-5-en-3-yl esters are described and discussed.

In a previous paper¹ we reported that solvolysis of 4,4-dimethyl-5 α -cholestan-3 β -yl toluene-*p*-sulphonate (I; R = *p*-C₆H₄Me·SO₂) gave the expected rearranged ring-contracted products (II, III), accompanied by the unrearranged alcohol or acetate with

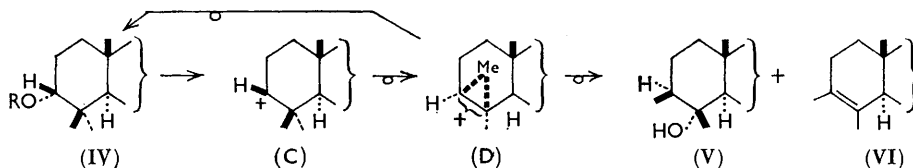
* Part L, *J.*, 1962, 1246.

¹ Shoppee and Johnston, *J.*, 1961, 3261.

retained configuration (I; R = H or Ac). The structures (II) and (III) were independently confirmed by Biellmann and Ourisson.²

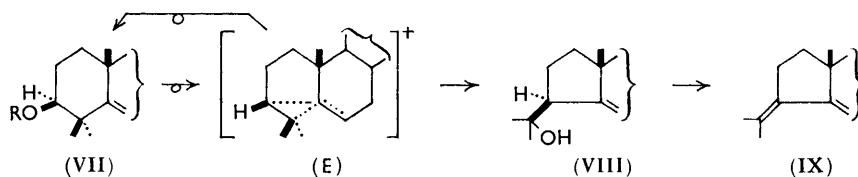


Similarly solvolysis of 4,4-dimethyl-5 α -cholestan-3 α -yl toluene-*p*-sulphonate (IV; R = *p*-C₆H₄Me·SO₂) gave the expected rearranged products without ring-contraction (V, VI), again accompanied by the unrearranged alcohol or acetate with retained configuration (IV; R = H or Ac). Kinetic study showed that these solvolyses are normal-



rate, unimolecular reactions (S_N1); synartetic acceleration (anchimeric assistance) is absent. To account for both the structural and the kinetic evidence, it was suggested that the rate-controlling ionisations produce the classical carbonium ions (A,C) (as intimate ion pairs), which rearrange to the more thermodynamically stable non-classical carbonium ions (B,D) at rates which are rapid compared with those of the initial heterolyses. Subsequent kinetic observations on the acetolysis of 4,4,14 α -trimethyl-5 α -cholesta-8,24-dien-3 β -yl and -3 α -yl toluene-*p*-sulphonate led to a similar conclusion.³

Solvolyses of 4,4-dimethylcholest-5-en-3 β -yl toluene-*p*-sulphonate (VII; R = *p*-C₆H₄Me·SO₂) disclose an interesting situation. In aqueous acetone (containing potassium acetate) the products^{4,5} are the rearranged, ring-contracted compounds (VIII, IX) accompanied by the unrearranged alcohol with retained configuration (VII; R = H); in acetic acid at 50°, the products^{4,5} are the Δ -nordiene (IX) and the unrearranged acetate with retained configuration (VII; R = Ac), but the rate⁴ ($10^4 k_1 = 960 \text{ min.}^{-1}$) is two-hundred times that¹ for the saturated analogue (I; R = *p*-C₆H₄Me·SO₂) ($10^4 k_1 = 4.8 \text{ min.}^{-1}$). There is thus synartetic acceleration by the π -electrons of the 5,6-double bond, but the product pattern conforms to that of the 5 α -series. It appears that there is direct formation of a mesomeric carbonium ion (E), which by reaction at C₍₃₎ and C₍₄₎ affords respectively the 3 β -alcohol (VII; R = H) and the rearranged tertiary alcohol (VIII), but which fails by



reaction at C₍₆₎ to furnish a 4,4-dimethyl-3 α ,5 α -cyclo-6 β -steroidal alcohol. The three canonical cationic structures contributing to the mesomeric carbonium ion (E)

² Biellmann and Ourisson, *Bull. Soc. chim. France*, 1960, 348.

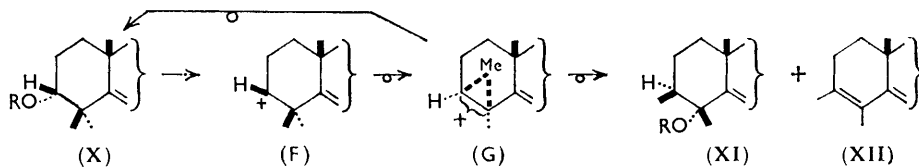
³ Bancroft, Haddad, and Summers, *J.*, 1961, 3295.

⁴ Moriarty and Wallis, *J. Org. chem.*, 1959, **24**, 1274, 1987.

⁵ Haddad and Summers, *J.*, 1959, 769.

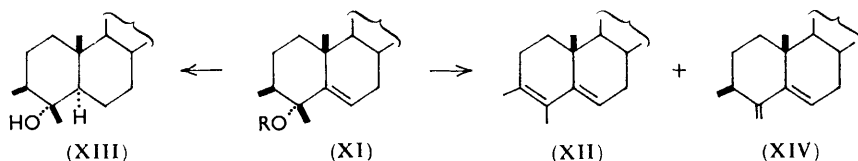
are respectively tertiary, secondary, and secondary, so that their relative thermodynamic stabilities would form a sequence: $C_{(3)}HR_2-C^+(4)R_2 > C^+(3)HR-C(4)R_3 > C_{(3)}HR_2-C_{(5)}R_2-C^+(6)HR$ corresponding with that for product formation at $C_{(4)} > C_{(3)} > C_{(6)}$.

It seemed appropriate to prepare, and examine the solvolysis of, the epimeric 4,4-dimethylcholest-5-en-3 α -yl toluene-*p*-sulphonate (X; R = *p*-C₆H₄Me·SO₂). 4,4-Dimethylcholest-5-en-3 α -ol (X; R = H) was readily obtained by Meerwein-Ponndorf reduction of 4,4-dimethylcholest-5-en-3-one⁶ and was characterised as the acetate. The molecular geometry of this system is unfavourable to intervention of the π -electrons of the Δ^5 -double bond,⁷ so that synartetic acceleration should not occur; conversely, the 3 α /4 β -*trans*-diaxial arrangement is favourable to participation by the σ -electrons of the 4 β -methyl group, leading to rearranged products and possibly to some small increase in rate.



4,4-Dimethylcholest-5-en-3 α -yl toluene-*p*-sulphonate (X; R = *p*-C₆H₄Me·SO₂), heated in aqueous acetone in the presence of sodium acetate for 60 hr., gave 4,4-dimethylcholest-5-en-3 α -ol (X; R = H) (10%), unaccompanied by the epimeric 3 β -alcohol (VII; R = H), but together with 3 β ,4 β -dimethylcholest-5-en-4 α -ol (XI; R = H) (4.5%) and 3,4-dimethylcholesta-3,5-diene (XII) (85%). 3 β ,4-Dimethylcholest-4-en-6 α -ol could not be isolated, and was not a product of the solvolysis. Acetolysis of the ester (X; R = *p*-C₆H₄Me·SO₂) in anhydrous acetic acid in the presence or absence of anhydrous sodium acetate at 95° for 3 hr. gave 4,4-dimethylcholest-5-en-3 α -yl acetate (X; R = Ac) (5%), unaccompanied by the epimeric 3 β -yl acetate (VII; R = Ac) or the tertiary 4 α -acetate (XI; R = Ac), but together with 3,4-dimethylcholesta-3,5-diene (XII) (95%).

3 β ,4 β -Dimethylcholest-5-en-4 α -ol (XI) resisted acetylation with acetic anhydride-pyridine at 100°; catalytic hydrogenation with platinum-acetic acid gave 3 β ,4 β -dimethyl-5 α -cholestan-4 α -ol (XIII),¹ whilst dehydration with phosphoryl chloride and pyridine at 95° yielded a mixture of 3,4-dimethylcholesta-3,5-diene (XII) and 3 β -methyl-4-methylenecholest-5-ene (XIV), which afforded formaldehyde on ozonolysis.



3,4-Dimethylcholesta-3,5-diene (XII), by hydrogenation with platinum-acetic acid at atmospheric pressure, gave 3 β ,4 β -dimethyl-5 α -cholestane (XV), also obtained by high-pressure hydrogenation of 3,4-dimethyl-5 α -cholest-3-ene (XVI).⁸ The saturated hydrocarbon (XV) was different from 4,4-dimethyl-5 α -cholestane (XIX), obtained by Wolff-Kishner reduction of 4,4-dimethylcholest-5-en-3-one (XVII)⁶ and subsequent catalytic hydrogenation of the intermediate 4,4-dimethylcholest-5-ene (XVIII) with platinum-acetic acid.

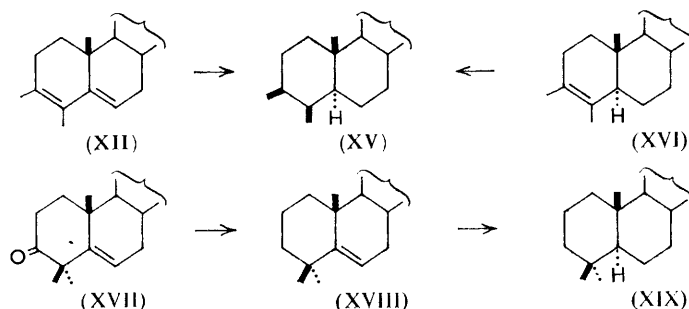
Owing to external circumstances, work had to be discontinued before a detailed kinetic

⁶ Woodward, Patchett, Barton, Ives, and Kelly, *J.*, 1957, 1131.

⁷ Shoppee and Williams, *J.*, 1955, 686.

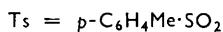
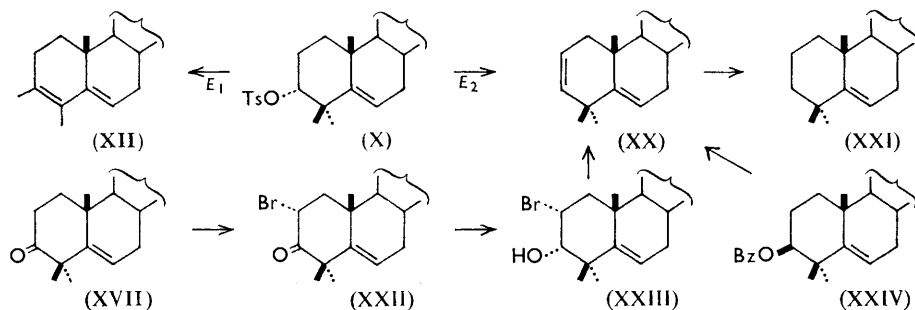
⁸ Beeton, Halsall, Jones, and Phillips, *J.*, 1957, 753.

study could be completed. The rate of solvolysis was however similar to those observed for the saturated 4,4-dimethyl-5 α -cholestan-3 β -yl and -3 α -yl toluene-*p*-sulphonates (I, IV; R = *p*-C₆H₄Me·SO₂) [$10^4k_1^{50} = 4.8 \text{ min.}^{-1}$ (ref. 1), $10^4k_1^{60} = 17.1 \text{ min.}^{-1}$ (ref. 1), $10^4k_1^{77} = 62.1 \text{ min.}^{-1}$ (ref. 3) for the 3 β -yl ester,* and $10^4k_1^{50} = 9.8 \text{ min.}^{-1}$ (ref. 1), $10^4k_1^{60} = 34.2$



min.⁻¹ (ref. 1), $10^4k_1^{77} = 171 \text{ min.}^{-1}$ (ref. 3) for the 3 α -yl ester*] and much slower than that of 4,4-dimethylcholest-5-en-3 β -yl toluene-*p*-sulphonate (VII; R = *p*-C₆H₄Me·SO₂); thus the Δ^5 -3 α -ester (X; R = *p*-C₆H₄Me·SO₂) requires 60 hr. for complete decomposition, whereas the Δ^5 -3 β -ester (VII; R = *p*-C₆H₄Me·SO₂) requires only 18 hr. for complete reaction under comparable conditions.^{4,5} We conclude that solvolysis of 4,4-dimethylcholest-5-en-3 α -yl toluene-*p*-sulphonate is unaccelerated, and that heterolysis affords a classical carbonium ion (F), which rearranges to the more thermodynamically stable non-classical carbonium ion (G) at a rate which is rapid compared with that of the initial ionisation [cf. (I) \rightarrow (A) \rightarrow (B), and (IV) \rightarrow (C) \rightarrow (D)].

Finally, we record some reactions of the epimeric Δ^5 -3-alcohols (VII, X; R = H) and their esters. Chromatography of 4,4-dimethylcholest-5-en-3 α -yl toluene-*p*-sulphonate (X; R = *p*-C₆H₄Me·SO₂) on aluminium oxide in pentane gave a mixture of 3,4-dimethylcholesta-3,5-diene (XII) and 4,4-dimethylcholesta-2,5-diene (XX), readily separable by



fractional crystallisation. The former arises by a unimolecular elimination (E_1) involving the carbonium ions (F) and (G), whilst the latter must be formed by *trans*-diaxial bimolecular elimination (E_2) involving the 2 β -hydrogen atom and the 3 α -toluene-*p*-sulphonate group.

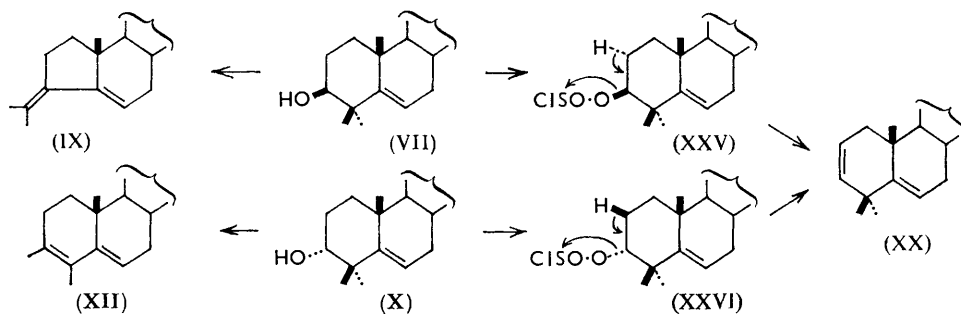
* These rates differ but little from those found for 5 α -cholestan-3 β -yl and -3 α -yl toluene-*p*-sulphonates, *viz.*, $10^4k_1^{50} = 0.65 \text{ min.}^{-1}$ (ref. 9), $10^4k_1^{75} = 17 \text{ min.}^{-1}$ (ref. 10), and $10^4k_1^{50} = 4.4 \text{ min.}^{-1}$ (ref. 9), $10^4k_1^{75} = 102 \text{ min.}^{-1}$ (ref. 10), respectively.

⁹ Winstein, personal communication.

¹⁰ Nishida, *J. Amer. Chem. Soc.*, 1960, **82**, 4290.

4,4-Dimethylcholesta-2,5-diene (XX) showed only rising end-absorption in the ultra-violet spectrum, whilst exhibiting maxima at 802 and 720 cm^{-1} in the infrared region. It was also prepared by two routes: (a) 4,4-dimethylcholest-5-en-3-one (XVII)⁶ by monobromination gave the 2 α -bromo-3-ketone (XXII)^{11,12} which with sodium borohydride furnished the 2 α -bromo-3 α -hydrin (XXIII), converted by *cis*-elimination of the elements of hypobromous acid¹³⁻¹⁵ with zinc-acetic acid into the 2,5-diene (XX); (b) 4,4-dimethylcholest-5-en-3 β -yl benzoate (XXIV), on pyrolysis, underwent *cis*-elimination of benzoic acid¹⁶ to give a poor yield of the 2,5-diene (XX). Partial hydrogenation of the 2,5-diene (XX) with platinum-acetic acid afforded 4,4-dimethylcholest-5-ene (XXI).

Dehydration of 4,4-dimethylcholest-5-en-3 β -ol (VII) by treatment with phosphorus pentachloride has been found⁵ to give 3-isopropylidene-A-norcholest-5-ene (IX); dehydration with thionyl chloride, however, produced, not only the rearranged A-nordiene (IX) by way of the carbonium ion (E), but also 4,4-dimethylcholesta-2,5-diene (XX), which appears to arise by *trans*-diequatorial bimolecular elimination (*E2*) from the intermediate 3 β -chlorosulphinat (XXV). If ring A of the 3 β -chlorosulphinat (XXV) passes into the boat conformation (a process possibly assisted by the 1,3-steric repulsions of the 4 β -methyl and 10 β -methyl groups), then the reaction becomes a *trans*-diaxial bimolecular elimination of the usual type.



Dehydration of 4,4-dimethylcholest-5-en-3 α -ol (X) with phosphorus pentachloride gave 3,4-dimethylcholesta-3,5-diene (XII) in good yield by way of the carbonium ions (F) and (G) *seriatim*; dehydration with thionyl chloride, however, furnished a mixture, consisting of the rearranged 3,5-diene (XII) and the unrearranged 2,5-diene (XX), which must arise by a *trans*-diaxial bimolecular elimination (*E2*) from the intermediate 3 α -chlorosulphinat (XXVI).

EXPERIMENTAL

For general experimental directions see *J.*, 1959, 345. M. p.s were determined on a Kofler block and are corrected. $[\alpha]_D$ refer to chloroform solutions at room temperature. Ultraviolet absorption spectra were determined for cyclohexane solutions, unless otherwise stated, on a 4000 A Perkin-Elmer model spectrophotometer. Infrared absorption spectra were measured for carbon tetrachloride solutions by use of a Perkin-Elmer model 221 spectrophotometer. Chromatography was on silica gel (Davison 40—200 mesh) or aluminium oxide (Spence's type H, activity II).

4,4-Dimethylcholest-5-en-3 α -ol.—4,4-Dimethylcholest-5-en-3-one (1.05 g.) in dry propan-2-ol

¹¹ Adams, Patel, Stuart-Webb, and Sturgeon, *J.*, 1956, 4490.

¹² Cropp, Dewhurst, and Holker, *Chem. and Ind.*, 1961, 7, 209.

¹³ James, Rees, and Shoppee, *J.*, 1955, 1370.

¹⁴ Barton, Lewis, and McGhie, *J.*, 1957, 2907.

¹⁵ Cornforth, Cornforth, and Mathew, *J.*, 1959, 112.

¹⁶ Barton, *J.*, 1949, 2174.

(100 c.c.) was refluxed for 6 hr. in the presence of aluminium isopropoxide (1.0 g.). The mixture was then slowly distilled until the distillate was free from acetone (~4 hr.), then poured into water (100 c.c.) and ether (100 c.c.), shaken, and acidified with dilute hydrochloric acid. Working up in the usual way gave crystals (1.04 g.), which were chromatographed on aluminium oxide (30 g.) in pentane. Elution with ether-pentane (1 : 19) gave 4,4-dimethylcholest-5-en-3 α -ol (345 mg.), having m. p. 144–145°, $[\alpha]_D -93^\circ$ (*c* 1.0) (crystallisation from ether-methanol) [Found (after drying at 85°/0.2 mm. for 24 hr.): C, 83.9; H, 12.05. C₂₉H₅₀O requires C, 84.5; H, 12.15%]. Treatment with acetic anhydride-pyridine overnight at 20° afforded 4,4-dimethylcholest-5-en-3 α -yl acetate, m. p. 111–112°, $[\alpha]_D -112^\circ$ (*c* 1.1) (crystallisation from methanol) [Found (after drying at 85°/0.2 mm. for 24 hr.): C, 81.5; H, 11.4. C₃₁H₅₂O₂ requires C, 81.5; H, 11.5%]. Elution with ether-pentane (1 : 9) gave 4,4-dimethylcholest-5-en-3 β -ol (685 mg.), m. p. 161–162°, $[\alpha]_D -68^\circ$ (*c* 1.0) (crystallisation from dry methanol) [Found (after drying at 85°/0.2 mm. for 24 hr.): C, 84.0; H, 11.9. Calc. for C₂₉H₅₀O: C, 84.0; H, 12.15%]. Woodward *et al.*⁶ report m. p. 150–151°, $[\alpha]_D -64^\circ$, for 4,4-dimethylcholest-5-en-3 β -ol prepared by reduction of 4,4-dimethylcholest-5-en-3-one with lithium aluminium hydride.

4,4-Dimethylcholest-5-en-3 α -yl Toluene-*p*-sulphonate.—4,4-Dimethylcholest-5-en-3 α -ol (200 mg.) in dry pyridine (5 c.c.) was treated at 0° with toluene-*p*-sulphonyl chloride (470 mg.). After 3 days at 25°, ice was added, and the mixture set aside for 1 hr. The product was extracted into ether and the extract washed with cold 2*N*-hydrochloric acid, water, 2*N*-sodium hydrogen carbonate, and to neutrality with water, dried (Na₂SO₄), and evaporated *in vacuo*. The solid residue (295 mg.) gave, after crystallisation from acetone, 4,4-dimethylcholest-5-en-3 α -yl toluene-*p*-sulphonate, m. p. 137–138°, $[\alpha]_D -87^\circ$ (*c* 0.9) [Found (after drying at 60°/0.2 mm. for 3 hr.): C, 76.2; H, 10.0. C₃₆H₅₆O₃S requires C, 76.0; H, 9.9%].

Solvolysis of 4,4-Dimethylcholest-5-en-3 α -yl Toluene-*p*-sulphonate in Aqueous Acetone.—4,4-Dimethylcholest-5-en-3 α -yl toluene-*p*-sulphonate (595 mg.) in acetone (25 c.c.) was treated with water (2.5 c.c.) and anhydrous sodium acetate (500 mg.) and refluxed for 60 hr. Most of the acetone was removed under reduced pressure, and the residue was extracted with ether, and worked up in the usual way to give white crystals (415 mg.). Chromatography on aluminium oxide (15 g.) in pentane and elution with pentane gave 3,4-dimethylcholesta-3,5-diene (353 mg., 85.5%), m. p. 100–101°, $[\alpha]_D -146^\circ$ (*c* 1.1), λ_{\max} 245 m μ ,¹⁷ ν_{\max} (in CS₂) 800 cm.⁻¹ (crystallisation from chloroform-methanol) [Found (after drying at 60°/0.2 mm. for 10 hr.): C, 87.7; H, 12.35. C₂₉H₄₈ requires C, 87.8; H, 12.2%]. Elution with ether-pentane (1 : 99) yielded 3 β ,4 β -dimethylcholest-5-en-4 α -ol (19 mg., 4.5%), m. p. 138–139°, $[\alpha]_D -21^\circ$ (*c* 0.6), ν_{\max} (in CS₂) 800 cm.⁻¹ (crystallisation from dry methanol) [Found (after drying at 60°/0.2 mm. for 10 hr.): C, 84.05; H, 12.0. C₂₉H₅₀O requires C, 84.0; H, 12.15%]. Treatment with acetic anhydride-pyridine at 25° for 1 week failed to bring about acetylation. Further elution with ether-pentane (1 : 99) gave 4,4-dimethylcholest-5-en-3 α -ol (41 mg., 10%), m. p. and mixed m. p. 144–145°, $[\alpha]_D -95^\circ$ (*c* 0.8) (crystallisation from ether-methanol), unaccompanied by the epimeric 3 β -ol.

Acetolysis of 4,4-Dimethylcholest-5-en-3 α -yl Toluene-*p*-sulphonate.—4,4-Dimethylcholest-5-en-3 β -yl toluene-*p*-sulphonate (570 mg.) in anhydrous acetic acid (70 c.c.) containing anhydrous sodium acetate (280 mg.) was heated at 95° for 3 hr. Removal of the solvent *in vacuo*, extraction with ether, and working up in the usual way gave a yellow oil, which was chromatographed on aluminium oxide (15 g.) in pentane. Elution with pentane gave 3,4-dimethylcholesta-3,5-diene (376 mg., 95%), m. p. and mixed m. p. 100–101°, $[\alpha]_D -145^\circ$ (*c* 0.9) (crystallisation from chloroform-methanol). Elution with ether-pentane (1 : 99) yielded 4,4-dimethylcholest-5-en-3 α -yl acetate (23 mg., 5%), m. p. and mixed m. p. 111–112°, $[\alpha]_D -110^\circ$ (*c* 0.9) (crystallisation from methanol), unaccompanied by the epimeric 3 β -yl acetate. Similar results were obtained in a second experiment without the sodium acetate buffer.

Hydrogenation of 3 β ,4 β -Dimethylcholest-5-en-4 α -ol.—The alcohol (10 mg.) in acetic acid (10 c.c.) was hydrogenated at atmospheric pressure in the presence of Adams catalyst (5 mg.). Removal of the catalyst and evaporation to dryness *in vacuo* yielded crystals. Recrystallisation from methanol gave 3 β ,4 β -dimethyl-5 α -cholestan-4 α -ol¹ (8 mg.), m. p. and mixed m. p. 145–147°.

Dehydration of 3 β ,4 β -Dimethylcholest-5-en-4 α -ol.—The alcohol (25 mg.) in pyridine (5 c.c.) was heated at 95° for 1 hr. with freshly distilled phosphoryl chloride (0.5 c.c.). Dilution with water and extraction with ether gave a yellow oil which was chromatographed on aluminium oxide (1 g.) in pentane. Elution with pentane afforded a mixture of dienes (20 mg.), m. p.

83—98°, $[\alpha]_D -100^\circ$ (c 0.5), ν_{\max} . (in CS_2) 885, 800 cm^{-1} (crystallisation from chloroform-methanol). Ozonolysis of this mixture (10 mg.) in carbon tetrachloride at -15° gave formaldehyde isolated as its 2,4-dinitrophenylhydrazone (1 mg.) by the procedure described by Shoppee and Johnston.¹

Hydrogenation of 3,4-Dimethylcholesta-3,5-diene.—The diene (136 mg.) in acetic acid (100 c.c.) was hydrogenated at atmospheric pressure in the presence of Adams catalyst (10 mg.). Filtration and removal of the solvent *in vacuo* gave a colourless oil which was chromatographed on aluminium oxide (3 g.) in pentane. Elution with pentane (100 c.c.) and crystallisation from acetone gave 3 β ,4 β -dimethyl-5 α -cholestane (115 mg.), m. p. 88—89°, $[\alpha]_D +9^\circ$ (c 1.1) [Found (after drying at 45°/0.2 mm. for 12 hr.): C, 87.0; H, 13.1. $\text{C}_{29}\text{H}_{52}$ requires C, 86.9; H, 13.1%]. The product gave no colour with tetranitromethane and did not exhibit "rising end-absorption" in the ultraviolet spectrum. The m. p. was depressed by *ca.* 10° on admixture with 4,4-dimethyl-5 α -cholestane, m. p. 86—87°.

Hydrogenation of 3,4-Dimethyl-5 α -cholest-3-ene.—3,4-Dimethyl-5 α -cholest-3-ene⁸ (30 mg.) in anhydrous acetic acid (50 c.c.) was hydrogenated at 1250 lb./sq. in. for 4 hr. at 135° in the presence of Adams catalyst (30 mg.). Filtration and removal of the solvent *in vacuo* gave a crystalline residue. Recrystallisation from acetone yielded 3 β ,4 β -dimethyl-5 α -cholestane (25 mg.), m. p. and mixed m. p. 88—89°.

4,4-Dimethylcholest-5-ene.—4,4-Dimethylcholest-5-en-3-one⁶ (250 mg.) in diethylene glycol (7 c.c.) was heated with 100% hydrazine hydrate (0.25 c.c.) at 200° (bath-temp.) for 30 min. The mixture was allowed to cool, a solution of sodium (0.25 g.) in diethylene glycol (2.5 c.c.) added, and the whole refluxed for a further 6 hr. The mixture was diluted with water, extracted with ether, and worked up in the usual way, to give 4,4-dimethylcholest-5-ene (198 mg.), m. p. 73—74°, $[\alpha]_D -73^\circ$ (c 1.1), ν_{\max} . (in CS_2) 799 cm^{-1} (crystallisation from chloroform-methanol) [Found (after drying at 35°/0.2 mm. for 24 hr.): C, 87.1; H, 12.8. $\text{C}_{29}\text{H}_{50}$ requires C, 87.4; H, 12.6%].

4,4-Dimethyl-5 α -cholestane.—4,4-Dimethylcholest-5-ene (45 mg.) in acetic acid (50 c.c.) was hydrogenated at atmospheric pressure in the presence of Adams catalyst (10 mg.). Filtration and removal of the solvent *in vacuo* gave a colourless oil. Crystallisation from methanol afforded 4,4-dimethyl-5 α -cholestane (37 mg.), m. p. 86—87°, $[\alpha]_D -8^\circ$ (c 0.8) [Found (after drying at 35°/0.2 mm. for 24 hr.): C, 87.0; H, 13.0. $\text{C}_{29}\text{H}_{52}$ requires C, 86.9; H, 13.1%].

Chromatography of 4,4-Dimethylcholest-5-en-3 α -yl Toluene-p-sulphonate on Aluminium Oxide.—4,4-Dimethylcholest-5-en-3 α -yl toluene-*p*-sulphonate (285 mg.) in pentane (30 c.c.) was chromatographed on aluminium oxide (10 g.) prepared in pentane. Elution with pentane (2 \times 30 c.c.) and crystallisation from chloroform-methanol gave a mixture of dienes (195 mg.), m. p. 85—89°. Fractional crystallisation of the mixture gave 3,4-dimethylcholesta-3,5-diene (45 mg.), m. p. and mixed m. p. 100—101°, as the less soluble fraction, and 4,4-dimethylcholesta-2,5-diene (85 mg.), m. p. 92—93°, $[\alpha]_D -37^\circ$ (c 1.2), ν_{\max} . (in CS_2) 802, 720 cm^{-1} , rising ultraviolet end-absorption, as the more soluble fraction [Found (after drying at 35°/0.2 mm. for 24 hr.): C, 87.6; H, 12.35. $\text{C}_{29}\text{H}_{48}$ requires C, 87.8; H, 12.2%].

Reduction of 2 α -Bromo-4,4-dimethylcholest-5-en-3-one by Sodium Borohydride.—2 α -Bromo-4,4-dimethylcholest-5-en-3-one^{11,12} (107 mg.) in dry methanol (50 c.c.) was treated with sodium borohydride (50 mg.) for 18 hr. at 25°. After dilution with water, acidification, extraction with ether, and working up in the usual way, the product crystallised from methanol to yield 2 α -bromo-4,4-dimethylcholest-5-en-3 α -ol (85 mg.), m. p. 114—115°, $[\alpha]_D -72^\circ$ (c 0.8), ν_{\max} . (in CS_2) 1060, 975, and 800 cm^{-1} [Found (after drying at 70°/0.2 mm. for 24 hr.): C, 70.0; H, 10.1. $\text{C}_{29}\text{H}_{49}\text{OBr}$ requires C, 70.1; H, 9.9%].

Treatment of 2 α -Bromo-4,4-dimethylcholest-5-en-3 α -ol with Zinc in Acetic Acid (cf. refs. 14, 15).—2 α -Bromo-4,4-dimethylcholest-5-en-3 α -ol (250 mg.) in acetic acid (25 c.c.) was refluxed with zinc dust (2 g.), added in small portions during 2 hr. Filtration, removal of the solvent *in vacuo*, extraction with ether, and working up in the usual way gave a yellow oil which was chromatographed on aluminium oxide (8 g.) in pentane. Elution with pentane and crystallisation from chloroform-methanol gave 4,4-dimethylcholesta-2,5-diene (110 mg.), m. p. and mixed m. p. 92—93°. Further elution with pentane and crystallisation from chloroform-methanol yielded 4,4-dimethylcholest-5-en-3-one⁶ (18 mg.), m. p. and mixed m. p. 176—177°. Elution with ether-pentane (1:99) gave 4,4-dimethylcholest-5-en-3 α -yl acetate (49 mg.), m. p. and mixed m. p. 111—112° (from methanol). Elution with ether-pentane (1:9) afforded 4,4-dimethylcholest-5-en-3 α -ol (21 mg.), m. p. and mixed m. p. 144—145° (from ether-methanol).

Hydrogenation of 4,4-Dimethylcholesta-2,5-diene.—4,4-Dimethylcholesta-2,5-diene (34 mg.) in acetic acid (25 c.c.) was partially hydrogenated at atmospheric pressure in the presence of Adams catalyst (30 mg.). Filtration and removal of the solvent *in vacuo* gave 4,4-dimethylcholest-5-ene (28 mg.), m. p. and mixed m. p. 73—74° (from chloroform-methanol).

4,4-Dimethylcholesta-2,5-diene from the Pyrolysis of 4,4-Dimethylcholest-5-en-3 β -yl Benzoate.—4,4-Dimethylcholest-5-en-3 β -ol (500 mg.; dried by azeotropic distillation with toluene) in dry pyridine (5 c.c.) and benzoyl chloride (1 c.c.) was kept at 95° for 1.5 hr. The solvent was removed under reduced pressure and the residue worked up in the usual way by ether-extraction. Crystallisation of the product from ether-methanol furnished 4,4-dimethylcholest-5-en-3 β -yl benzoate (485 mg.), m. p. 139—140°, $[\alpha]_D^{20}$ -23° (c 1.1) [Found (after drying at 75°/0.2 mm. for 12 hr.): C, 83.65; H, 10.5. $C_{36}H_{54}O_2$ requires C, 83.3; H, 10.5%]. This benzoate (115 mg.) was heated under reflux for 1 hr. in an atmosphere of nitrogen. The resulting clear oil was chromatographed on aluminium oxide (3 g.) in pentane. Elution with pentane gave 4,4-dimethylcholesta-2,5-diene (28 mg.), m. p. and mixed m. p. 92—93°.

Treatment of 4,4-Dimethylcholest-5-en-3 α -ol with Phosphorus Pentachloride in Benzene.—4,4-Dimethylcholest-5-en-3 α -ol (100 mg.) in dry benzene (15 c.c.) was treated at room temperature with freshly sublimed phosphorus pentachloride (50 mg.) for 2 hr. with stirring. Dilution with water, extraction into ether, and working up in the usual way gave a colourless oil. Filtration through aluminium oxide (3 g.) in pentane (100 c.c.) and removal of the solvent *in vacuo* afforded 3,4-dimethylcholesta-3,5-diene (85 mg.), m. p. and mixed m. p. 100—101° (from chloroform-methanol).

Treatment of 4,4-Dimethylcholest-5-en-3 α -ol with Thionyl Chloride in Benzene.—4,4-Dimethylcholest-5-en-3 α -ol (100 mg.) in dry benzene (15 c.c.) was heated under reflux with freshly distilled thionyl chloride (0.5 c.c.) for 2 hr. Removal of the solvent *in vacuo*, extraction of the residue with ether, and working up in the usual way gave a yellow oil. Filtration through aluminium oxide (3 g.) in pentane (100 c.c.) and removal of the solvent *in vacuo* gave crystals (88 mg.). Fractional crystallisation from chloroform-methanol gave 4,4-dimethylcholesta-2,5-diene (65 mg.), m. p. and mixed m. p. 92—93°, and 3,4-dimethylcholesta-3,5-diene (8 mg.), m. p. and mixed m. p. 100—101°.

Treatment of 4,4-Dimethylcholest-5-en-3 β -ol with Thionyl Chloride in Benzene.—4,4-Dimethylcholest-5-en-3 β -ol (100 mg.), treated as above for the 3 α -alcohol, gave a mixture (85 mg.) separated by fractional crystallisation from chloroform-methanol into 3-isopropylidene- Δ -norcholest-5-ene⁵ (36 mg.), m. p. and mixed m. p. 83—85°, and 4,4-dimethylcholesta-2,5-diene (31 mg.), m. p. and mixed m. p. 92—93°.

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