FISSION OF THE EPIMERIC 2,3-EPOXIDES IN THE 5,7β-CYCLO-B-HOMO-5β-CHOLESTANE SERIES*

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Cleavage of the epimeric 2,3-epoxide of the 5,7β-cyclo-B-homo-5β-cholestane series with hydrobromic acid has been studied. Chemical as well as spectral evidence of the structures of the compounds obtained is presented.

In connection with our studies on steroids with modified skeleton 2,3-disubstituted derivatives of the 5,7β-cyclo-B-homo-5β-cholestane series became of interest.

For introducing the two substituents in the required positions we made use of the already known[1] olefin *I*. Peracid epoxidation afforded a mixture of two epimeric epoxides in which the polar one predominated. The lipophilic epoxide was identical with the authentic[1] β-epoxide *III* and the main product of epoxidation is therefore the new α-epoxide *II*. Each epoxide on cleavage with hydrobromic acid afforded one single bromohydrin, the structures of which follow from spectral as well as chemical evidence: The α-epoxide *II* yielded the bromohydrin *IV* which represents the expected product of diaxial opening of the epoxide ring. When this bromohydrin was oxidised with Jones' reagent the reaction was accompanied by inversion of the bromine atom as follows from subsequent reactions and the stable 2α-bromo ketone *V* was obtained; this is in analogy to the normal 5α-steroid series[2-4] where the 2β-bromo-3-ketone is extremely unstable. Bromo ketone *V* on hydride reduction afforded the known bromohydrin *VI* and the new bromohydrin *IX*; both of them yielded the starting bromo ketone *V* on oxidation with Jones' reagent and they differ therefore in configuration of the hydroxyl group at $C_{(3)}$. Final proof of structure was provided by alkali treatment: Bromohydrin *IX* afforded the 3-oxocompound *VIII* which was also obtained from the bromo ketone *V* on catalytic dehalogenation. In addition, the bromohydrin *IX* gave the known[5] alcohol *XI* on debromination.

Bromination of the ketone *VIII* with Jacques' reagent afforded the stable bromo ketone *V* or the dibromo derivative *X* depending on the reaction conditions. Bromi-

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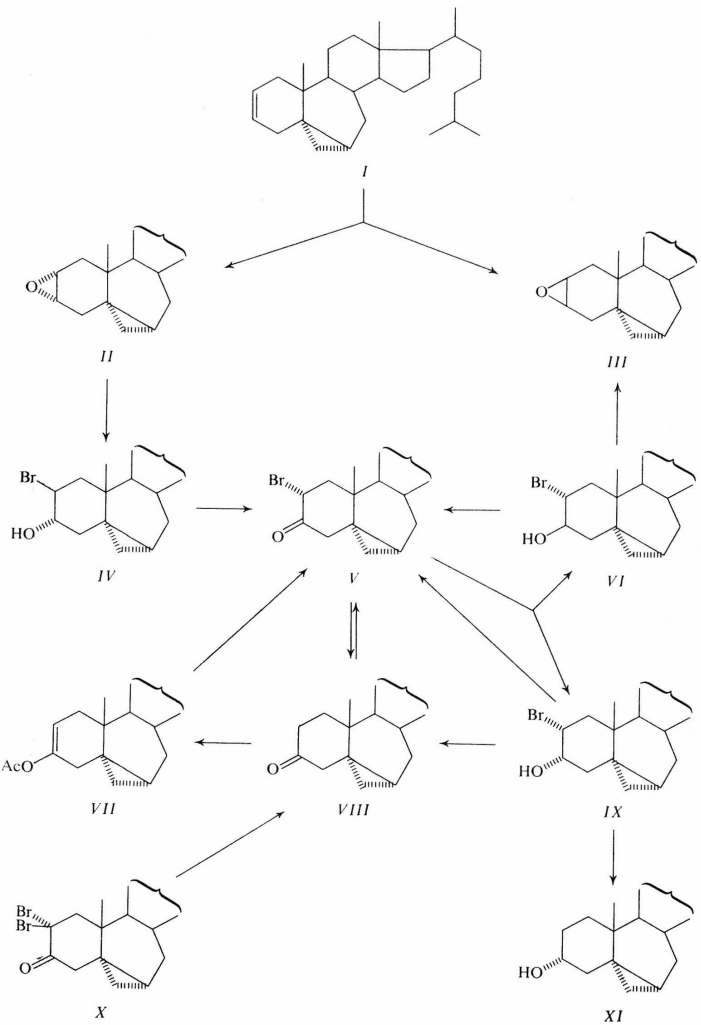
I
II
III
IV
V
VI
VII
VIII
IX
X
XI
Br
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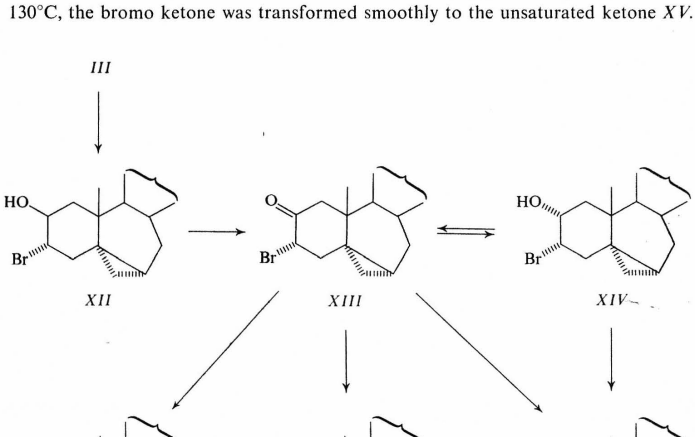
nation of the enol acetate *VII* with bromine yielded again the bromo ketone *V* as the sole product.

Cleavage of the β-epoxide *III* with hydrobromic acid afforded the known[1] bromohydrin *XII* as the sole product of diaxial opening. This bromohydrin was oxidised with Jones' reagent to the bromo ketone *XIII* which on reduction with sodium borohydride gave a new bromohydrin. Its structure follows from subsequent reactions: Alkali treatment led to the ketone *XVII* and oxidation yielded the starting bromo ketone *XIII*. This bromohydrin is therefore 2α-hydroxy-3α-bromo derivative *XIV*.

In further experiments the bromo ketone *XIII* was submitted to dehydrobromination reactions. When treated with lithium bromide in N,N-dimethylformamide at 130°C, the bromo ketone was transformed smoothly to the unsaturated ketone *XV*.



Dehydrohalogenation with *sym*-collidine gave somewhat complicated results. Mild conditions led to the inverted bromo ketone *XVI* with some starting material left unchanged, vigorous conditions afforded a mixture of some starting material, unsaturated ketone *XV*, inverted bromo ketone *XVI*, and a product of reductive debromination – ketone *XVII*. Analogous reaction has been observed in the normal steroid series where the 5α-cholestan-2-one was the sole product[6]. Perhaps in our case the cyclopropane ring supports formation of the conjugated system.

EXPERIMENTAL

Melting points were determined on a Kofler block. Optical activity measurements were carried out in chloroform with an error of $\pm 3°$. The infrared spectra were recorded on the Zeiss UR 20 spectrometer in tetrachloromethane unless otherwise stated. The ^{1}H-NMR spectra were recorded on the Tesla 60 MHz instrument in deuteriochloroform and corrected to tetramethylsilane (7·25 ppm) unless otherwise stated. The chemical shift is given in ppm. The identity of samples prepared by different routes was checked by mixture melting point determination, by thin layer chromatography (TLC), by infrared spectra and by ^{1}H-NMR spectra. Usual working up of a solution implies washing the solution with 5% aqueous hydrochloric acid, water, 5% aqueous potassium hydrogen carbonate solution, water, drying with sodium sulphate, and evaporation of the solvent *in vacuo*. Light petroleum refers to the fraction of b.p. 40–60°C.

2α,3α-Epoxy-5,7β-cyclo-B-homo-5β-cholestane (*II*)

Elution of the chromatography after isolation of the epoxide *III* with light petroleum–ether (49 : 1) afforded fractions with the polar epoxide. Working up gave 455 mg of a residue which was crystallised from methanol to yield 305 mg of the epoxide *II*, m.p. 144–146°C, $[\alpha]_D^{20}$ −45·7° (*c* 1·36). IR spectrum: 3070 cm^{-1} (cyclopropane). ^{1}H-NMR (100 Varian MHz instrument): 0·16 to 0·50 (mt, two cyclopropane protons), 0·59 (s, 18-H), 0·84 (d, J = 6 Hz, 26- and 27-H), 0·87 (d, J = 5·5 Hz, 21-H), 1·04 (s, 19-H). For $C_{28}H_{46}O$ (398·6) calculated: 84·35% C, 11·63% H; found: 84·55% C, 11·71% H.

2β,3β-Epoxy-5,7β-cyclo-B-homo-5β-cholestane (*III*)

The olefin *I* (480 mg) in dichloromethane (10 ml) was treated with *m*-chloroperbenzoic acid (480 mg) and allowed to stand at room temperature overnight. The mixture was diluted with water, the product taken into ether, and the excess peracid was removed by extraction with 5% sodium carbonate solution. The organic solution was washed with water, dried, and the solvent was distilled off. The residue (490 mg) was chromatographed on a silica gel column (100 g) in light petroleum–ether (49 : 1). Fractions with lipophilic product were combined and evaporated. The solid (9 mg) was crystallised from methanol to yield 2·5 mg of the epoxide *III*, m.p. 108 to 109°C, identical in all respects with the authentic[1] compound.

2β-Bromo-5,7β-cyclo-B-homo-5β-cholestan-3α-ol (*IV*)

A solution of the epoxide *II* (200 mg) in chloroform (10 ml) was treated with 48% hydrobromic acid (1·2 ml) and agitated for 30 min. The mixture was poured into water, and the product extracted into ether. The ethereal solution was washed with 5% sodium hydrogen carbonate solution, water, dried, and solvent removed. The residue (159 mg) was purified by preparative thin layer chromatography in light petroleum–ether (9 : 1) to yield after working up of the corresponding zones 86 mg of the bromohydrin *IV*, m.p. 100–102°C, $[\alpha]_D^{20}$ +11·5° (*c* 2·43). IR spectrum: 3628, 3617 (free hydroxyl), 3601, 3578 (bonded hydroxyl), 3065 cm^{-1} (cyclopropane). ^{1}H-NMR spectrum: from 0·39 (cyclopropane protons), 0·61 (s, 18-H), 0·86 (d, J = 5·5 Hz, 26- and 27-H), 0·91 (d, J = 5 Hz, 21-H), 1·22 (s, 19-H), 2·09 (s, OH), 4·35 (two mt, 2α-H and 3β-H). For $C_{28}H_{47}BrO$ (479·6) calculated: 70·12% C, 9·88% H, 16·66% Br; found: 70·20% C, 9·89% H, 16·25% Br.

2α-Bromo-5,7β-cyclo-B-homo-5β-cholestan-3-one (*V*)

a) *From* 5,7β-*cyclo*-B-*homo*-5β-*cholestan*-3-*one* (VIII): A solution of the ketone *VIII* (300 mg) in tetrahydrofuran (6 ml) was treated with Jacques' reagent (300 mg) and allowed to stand at room temperature for 5 min. The mixture was diluted with water, the product taken into ether, and the ethereal solution was washed with 5% sodium hydrogen carbonate solution, water, dried, and ether removed. The residue (370 mg) was chromatographed over silica gel (60 g) in light petroleum–ether (49 : 1). Working up of the corresponding fractions afforded 320 mg of a product which on crystallisation from acetone–water gave 180 mg of the ketone *V*, m.p. 130–131°C, $[\alpha]_D^{20}$ +7° (*c* 2·13) in accordance with the literature[7].

b) *From* 3β-*bromo*-5,7β-*cyclo*-B-*homo*-5β-*cholestan*-3α-*ol* (IV): The bromohydrin *IV* (15 mg) in acetone (2 ml) was treated with excess Jones' reagent and allowed to stand at room temperature for 5 min. The excess reagent was removed with methanol, the reaction mixture was diluted with water, and the product extracted with ethyl acetate. The organic layer was washed with 5% sodium hydrogen carbonate solution, water, dried, and solvent distilled off. The residue was purified by preparative TLC in light petroleum–ether (9 : 1) to yield 11 mg of a crude product which on crystallisation from methanol gave 3 mg of the bromo ketone *V*, m.p. 127–130°C, $[\alpha]_D^{20}$ +6·6° (*c* 1·19).

c) *From* 2α-*bromo*-5,7β-*cyclo*-B-*homo*-5β-*cholestan*-3α-*ol* (IX): The bromohydrin *IX* (160 mg) in acetone (30 ml) was oxidised with Jones' reagent as described under *b*). The ethyl acetate solution afforded after removal of the solvent 160 mg of a product which was purified by crystallisation from acetone–water. Yield 109 mg of the bromo ketone *V*, m.p. 133–134°C, $[\alpha]_D^{20}$ +5° (*c* 2·09).

d) *From* 2α-*bromo*-5,7β-*cyclo*-B-*homo*-5β-*cholestan*-3β-*ol* (VI): The bromohydrin *VI* (45 mg) in acetone (5 ml) was oxidised with Jones' reagent as described under *b*). The crude product (42 mg) was purified by preparative TLC in benzene to yield 29 mg of a product which on crystallisation from acetone–water afforded 16 mg of the bromo ketone *V*, m.p. 130–132°C, $[\alpha]_D^{20}$ +5° (*c* 1·12).

e) *From* 3-*acetoxy*-5,7β-*cyclo*-B-*homo*-5β-*cholest*-2-*ene* (VII): A solution of the enol acetate *VII* (50 mg) in tetrachloromethane (3 ml) was treated with a solution of bromine (20 mg) in the same solvent (2 ml). After 30 min at room temperature the mixture was poured in water, and the product isolated with ether. The ethereal solution was washed with a sodium thiosulphate solution, 5% potassium hydrogen carbonate solution, water, and dried. Evaporation of the solvent left 55 mg of a product which was crystallised from acetone–water to yield 33 mg of the bromo ketone *V*, m.p. 129–131°C, $[\alpha]_D^{20}$ +7° (*c* 1·19).

2α-*Bromo*-5,7β-*cyclo*-B-*homo*-5β-*cholestan*-3β-ol (VI)

The zones with the polar product after PLC of the bromohydrin IX afforded after working up 65 mg of a product which on crystallisation from methanol gave 32 mg of the bromohydrin *VI*, m.p. 55–58°C, $[\alpha]_D^{20}$ −37° (*c* 0·91). IR spectrum: 3570 (hydroxyl), 3060 cm^{-1} (cyclopropane). ^{1}H-NMR spectrum (Varian 100 MHz-instrument): 0·05 to 0·50 (mt, two cyclopropane protons), 0·58 (s, 18-H), 0·83 (d, $J = 6$ Hz, 26-H and 27-H), 0·86 (d, $J = 6$ Hz, 21-H), 1·08 (s, 19-H), 3·72 (mt, 3α-H), 4·32 (mt, 2β-H). For $C_{28}H_{47}BrO$ (479·6) calculated: 70·12% C, 9·88% H, 16·66% Br; found: 70·40% C, 9·81% H, 16·70% Br.

3-Acetoxy-5,7β-cyclo-B-homo-5β-cholest-2-ene (*VII*)

The ketone *VIII* (800 mg) was dried azeotropically with benzene, dissolved in isopropenyl acetate (10 ml), and treated with a solution of conc. sulphuric acid (0·06 ml) in isopropenyl acetate (1 ml). In the course of 1 h 4 ml of the reaction mixture were distilled off, 10 ml of isopropenyl acetate with sulphuric acid (0·1 ml) were added, and 9 ml of the mixture were distilled off within 1 h. The reaction mixture was diluted with light petroleum (200 ml) and filtered over an alumina column (alkal.; act. 1). The column was washed with the same solvent. After removal of the solvent the product (800 mg) was crystallised from ethanol to yield 520 mg of the enol acetate *VII*, m.p. 73–74°C, $[\alpha]_D^{20}$ +2° (*c* 0·92). IR spectrum: 3060 (cyclopropane), 1758, 1221 (acetate), 1690 cm^{-1} (double bond). ^{1}H-NMR spectrum (Varian 100 MHz-instrument): 0·15 to 0·40 (mt, two cyclopropane protons), 0·60 (s, 18-H), 0·83 (d, J = 6 Hz, 26-H and 27-H), 0·87 (d, J = 6 Hz, 21-H), 1·08 (s, 19-H), 2·04 (s, 3-acetate), 5·27 (mt, 2-H). For $C_{30}H_{48}O_2$ (440·7) calculated: 81·76% C, 10·98% H; found: 81·82% C, 10·90% H.

5,7β-Cyclo-B-homo-5β-cholestan-3-one (*VIII*)

a) *From* 3α-*bromo*-5,7β-*cyclo*-B-*homo*-5β-*cholestan*-3-*one* (V): The bromo ketone *V* (35 mg) in ethyl acetate (5 ml) and ethanol (2 ml) was agitated in a hydrogen atmosphere over 5% Pd/$CaCO_3$ catalyst for 2 h at room temperature. The catalyst was filtered off, washed with ether, the solvents were removed under reduced pressure and the residue was purified by preparative TLC in light petroleum–ether (9 : 1). Working up of the corresponding zones gave 27 mg of a product which was crystallised from methanol to yield 18 mg of the ketone *VIII*, m.p. 148–150°C, $[\alpha]_D^{20}$ −8° (*c* 1·16) in accordance with the literature[5].

b) *From* 2α-*bromo*-5,7β-*cyclo*-B-*homo*-5β-*cholestan*-3α-*ol* (IX): A solution of the bromohydrin *IX* (55 mg) and potassium hydroxide (200 mg) in methanol (20 ml) was refluxed for 30 min. The mixture was poured into water and the product isolated with ether in the usual way. The residue (41 mg) after evaporation of the solvent was crystallised from methanol to afford 20 mg of the ketone *VIII*, m.p. 148 to 149°C, $[\alpha]_D^{20}$ −14° (*c* 0·72).

2α-Bromo-5,7β-cyclo-B-homo-5β-cholestan-3α-ol (*IX*)

A solution of the bromo ketone *V* (200 mg) in ethanol (50 ml) was treated with sodium borohydride (400 mg) and allowed to stand at room temperature for 20 min. The excess hydride was destroyed with acetic acid, the mixture diluted with water, and the product taken into ether. The ethereal layer was worked up and the residue (200 mg) was purified by preparative TLC in light petroleum–ether (9 : 1). The zones with the lipophilic product were combined, and the product extracted with ether. The residue (100 mg) was crystallised from methanol to yield 63 mg of the bromohydrin *IX*, m.p. 136–137°C, $[\alpha]_D^{20}$ −23° (*c* 1·41). IR spectrum: 3565 (hydroxyl), 3070 cm^{-1} (cyclopropane). ^{1}H-NMR spectrum (Varian 100 MHz-instrument): 0·40 to 0·65 (mt, two cyclopropane protons), 0·58 (s, 18-H), 0·83 (d, J = 6 Hz, 26-H and 27-H), 0·86 (d, J = 6 Hz, 21-H), 1·06 (s, 19-H), 4·03 (mt, 3β-H), 4·62 (mt, 2β-H). For $C_{28}H_{47}BrO$ (479·6) calculated: 70·12% C, 9·88% H, 16·66% Br; found: 70·49% C, 9·77% H, 16·43% Br.

2α,2β-Dibromo-5,7β-cyclo-B-homo-5β-cholestan-3-one (*X*)

The ketone *VIII* (300 mg) in tetrahydrofuran (10 ml) was treated with Jacques' reagent (600 mg) and allowed to stand at room temperature for 20 min. The mixture was poured into water, and the product taken into ether. The ethereal solution was washed with 5% potassium hydrogen car-

bonate, 5% sodium thiosulphate, water, dried, and solvent removed. The crude product (320 mg) was chromatographed on a silica gel column (30 g) in light petroleum–ether (33 : 1). Working up of the corresponding fractions afforded 220 mg of a product which was crystallised from diluted acetone to yield 165 mg of the dibromo ketone *X*, m.p. 86–88°C, $[\alpha]_D^{20}$ +54° (*c* 1·52). IR spectrum: 3065 (cyclopropane), 1737 cm^{-1} (carbonyl). ^{1}H-NMR spectrum (Varian 100 MHz instrument): 0·29 (dd) and 0·44 (broad t, two cyclopropane protons), 0·62 (s, 18-H), 0·85 (d, J = 6 Hz, 26-H and 27-H), 0·88 (d, J = 6 Hz, 21-H), 1·47 (s, 19-H), 2·89 and 3·26 (two d, J = 15·5 Hz, 1-H), 1·61 (d, J = 15·5 Hz) and 3·62 (br d, J = 15·5 Hz, 4-H). For $C_{28}H_{44}BrO_2$ (556·5) calculated: 60·43% C, 7·97% H, 28·72% Br; found: 60·27% C, 8·14% H, 29·08% Br.

5,7β-Cyclo-B-homo-5β-cholestan-3α-ol (*XI*)

The bromohydrin *IX* (46 mg) in ethanol (5 ml) and ethyl acetate (5 ml) was agitated in a hydrogen atmosphere over 5% $Pd/CaCO_3$ catalyst (200 mg) at room temperature for 16 h. The catalyst was filtered off, washed with ether, and the residue (40 mg) was after evaporation of the solvents purified by preparative TLC in light petroleum–ether (3 : 1). Working up of the corresponding zones afforded 26 mg of the lipophilic starting material and 17 mg of the polar product which on crystallisation from acetone yielded 7 mg of the alcohol *XI*, m.p. 123–124°C, $[\alpha]_D^{20}$ −55° (*c* 1·19) in accordance with the literature[5].

3α-Bromo-5,7β-cyclo-B-homo-5β-cholestan-2β-ol (*XII*)

A solution of the epoxide *III* (300 mg) in chloroform (15 ml) was agitated with 48% hydrobromic acid (1·5 ml) at room temperature for 45 min. The mixture was poured into water, the product was extracted with chloroform, the extract was washed with potassium hydrogen carbonate, water, dried, and solvent distilled off. The residue (320 mg) was crystallised from methanol to yield 135 mg of the bromohydrin *XII*, m.p. 141–143°C, $[\alpha]_D^{20}$ −7° (*c* 1·18) in accordance with the literature[1].

3α-Bromo-5,7β-cyclo-B-homo-5β-cholestan-2-one (*XIII*)

a) *From* 5,7β-*cyclo*-B-*homo*-5β-*cholestan*-2-*one* (XVII): The ketone *XVII* (22 mg) in tetrahydrofuran (5 ml) was brominated with Jacques' reagent (44 mg). After 20 min at room temperature the mixture was poured into water, and the product extracted with ether. The ethereal solution was washed with a potassium hydrogen carbonate solution, water, dried, and the solvent removed. The residue was purified by preparative TLC in light petroleum–ether (5 : 1). The product obtained after working up of the zones was crystallised from ethanol to afford 13 mg of the bromo ketone *XIII*, m.p. 162 to 166°C, $[\alpha]_D^{20}$ −62° (*c* 1·19). IR spectrum: 3070 (cyclopropane), 1711 cm^{-1} (carbonyl). ^{1}H-NMR spectrum (Varian 100 MHz instrument): 0·595 (s, 18-H), 0·85 (d, J = 6·5 Hz, 26-H and 27-H), 0·875 (d, J = 6 Hz, 21-H), 0·96 (s, 19-H), 2·36 (br d, J = = 13 Hz) and 2·87 (br d, J = 13 Hz, 1-H), 2·80 (dd, J = 15·5 Hz, J' = 5 Hz, one 4-H), 4·30 (br d, J = 5 Hz, $J' \leqq 2$ Hz, 3β-H). For $C_{28}H_{45}BrO$ (477·6) calculated: 70·41% C, 9·50% H, 16·73% Br; found: 70·46% C, 9·68% H, 16·62% Br.

b) *From* 3α-*bromo*-5,7β-*cyclo*-B-*homo*-5β-*cholestan*-2β-*ol* (XII): The bromohydrin *XII* (300 mg) in acetone (100 ml) was oxidised with excess Jones' reagent. After 10 min at room temperature the excess oxidising agent was removed with methanol, the product precipitated with water, taken into ether, and the ethereal solution was worked up. Ether was removed and the residue (300 mg) was crystallised from ethanol to yield 236 mg of the bromo ketone *XIII*, m.p. 164–167°C, $[\alpha]_D^{20}$ −65° (*c* 1·47).

c) *From* 3α-*bromo*-5,7β-*cyclo*-B-*homo*-5β-*cholestan*-2α-*ol* (XIV): The bromohydrin *XIV* (45 mg) in acetone (5 ml) was oxidised with Jones' reagent as described in the previous experiment. Similar working up and crystallisation from ethanol gave 30 mg of the bromo ketone *XIII*, m.p. 163–166°C, $[\alpha]_D^{20}$ −63° (*c* 1·12).

3α-Bromo-5,7β-cyclo-B-homo-5β-cholestan-2α-ol (*XIV*)

A solution of the bromo ketone *XIII* (80 mg) in methanol (100 ml) was treated at 40°C with sodium borohydride (800 mg) and allowed to stand at the same temperature for 5 min. The mixture was then refluxed for 30 min, poured into water, and the excess hydride was decomposed with 5% hydrochloric acid. The product was extracted into ether, and the ethereal solution was worked up. The residue after evaporation of the solvent was purified by preparative TLC in light petroleum–ether (5 : 1). Working up of the corresponding zones afforded 62 mg of a product which on crystallisation from methanol gave 43 mg of the bromohydrin *XIV*, m.p. 147–150°C, $[\alpha]_D^{20}$ −26° (*c* 0·84). IR spectrum: 3560, 1067, 1060 (hydroxyl), 3080 cm^{-1} (cyclopropane). ^{1}H-NMR spectrum: 0·62 (s, 18-H), 0·86, (d, J = 5·5 Hz, 26-H and 27-H), 0·89 (d, J = 5 Hz, 21-H), 1·08 (s, 19-H), 3·74 (mt, $W_{1/2}$ = 21 Hz, 2β-H), 4·74 (mt, $W_{1/2}$ = 11 Hz, 3β-H). For $C_{28}H_{47}BrO$ (479·6) calculated: 70·12% C, 9·88% H, 16·66% Br; found: 70·40% C, 9·89% H, 17·30% Br.

5,7β-Cyclo-B-homo-5β-cholest-3-en-2-one (*XV*)

a) *From* 3α-*bromo*-5,7β-*cyclo*-B-*homo*-5β-*cholestan*-2-*one* (XIII) *with lithium bromide*: A solution of the bromo ketone *XIII* (180 mg) in N,N-dimethylformamide (4 ml) was heated with lithium bromide (180 mg) and lithium carbonate (180 mg) to 130°C for 26 h. The mixture was poured in water, and the product extracted with ether, and then with chloroform. The organic extracts were combined and worked up. The crude product (200 mg) was purified by preparative TLC in light petroleum–ether (9 : 1). The corresponding zones were worked up to yield 80 mg of a product which after crystallisation from methanol afforded 55 mg of the ketone *XV*, m.p. 133–134°C, $[\alpha]_D^{20}$ −190° (*c* 1·66) in agreement with the literature[1].

b) *From* XIII *with* sym-*collidine*: The zones with the most polar compound from the preparative TLC of the product from the following experiment under *b*) afforded after working up 23 mg of a crude product. Crystallisation from methanol gave 14 mg of the conjugated ketone *XV*, m.p. 131–134°C, $[\alpha]_D^{20}$ −187° (*c* 1·16).

3β-Bromo-5,7β-cyclo-B-homo-5β-cholestan-2-one (*XVI*)

a) The bromo ketone *XIII* (24 mg) in sym-collidine (5 ml) was refluxed for 30 min. The mixture was diluted with water, the product extracted with ethyl acetate, and the organic solution was worked up. The product was purified by preparative TLC in light petroleum–ether (9 : 1). Working up of the zones afforded 6 mg of the starting material and 10·5 mg of the epimeric bromo ketone *XVI*, m.p. 127–128°C (methanol), $[\alpha]_D^{20}$ −19° (*c* 1·32). IR spectrum: 3065 (cyclopropane), 1731 cm^{-1} (carbonyl). ^{1}H-NMR spectrum [HMDS (0·06 ppm) as internal standard]: 0·60 s, 18-H, 0·85 (d, J = 5 Hz, 26-H and 27-H), 0·88 (d, J = 5 Hz, 21-H), 1·03 (s, 19-H). For $C_{28}H_{45}$·.BrO (477·6) calculated: 70·41% C, 9·50% H, 16·73% Br; found: 70·45% C, 9·62% H, 16·13% Br.

b) The bromoketone *XIII* (68 mg) in *sym*-collidine (5 ml) was refluxed in a nitrogen atmosphere for 8 h. The mixture which was worked up as described under *a*) contained — according to the TLC — next to the starting material ketones *XV*, *XVI*, and *XVII*. Preparative TLC afforded the most lipophilic of these ketones, the bromo ketone *XVI*, m.p. 125–127°C (methanol; 11 mg).

5,7β-Cyclo-B-homo-5β-cholestan-2-one (*XVII*)

a) *From* XIII *on hydrogenation*: The bromo ketone *XIII* (50 mg) in ethyl acetate (5 ml) and ethanol (1·5 ml) was hydrogenated over 5% $Pd/CaCO_3$ (25 mg) for 2 h at room temperature. The catalyst was filtered off, washed with ether, and solvents removed. The residue was crystallised from methanol to yield 26 mg of the ketone *XVII*, m.p. 137—139°C, $[\alpha]_D^{20}$ —37° (*c* 1·12) in accordance with the literature[1].

b) *From* XIII *with* sym-*collidine*: Preparative TLC of the reaction product from the previous experiment under *b*) afforded zones with the bromo ketone *XVII*. Working up and crystallisation from methanol gave 7·5 mg of the compound, m.p. 134—137°C, $[\alpha]_D^{20}$ —32° (*c* 1·11).

c) *From* 3α-*bromo*-5,7β-*cyclo*-B-*homo*-5β-*cholestan*-2α-*ol* (XIV): The bromohydrin *XIV* *XIV* (30 mg) in methanol (10 ml) was refluxed with potassium hydroxide (100 mg) for 1 h. The mixture was diluted with water, and the product taken into ethyl acetate. Working up and evaporation of the solvent left 22 mg of a residue which on crystallisation from methanol gave 9 mg of the ketone *XVII*, m.p. 137—138°C, $[\alpha]_D^{20}$ —40° (*c* 1·16).

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