REACTION OF 5-BROMO-6β-CHLORO-5α-CHOLESTAN-3β-OL WITH SILVER SALTS

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Compound *IV* reacts with silver perchlorate and tetrafluoroborate predominantly under formation of rearranged products *XII*, *XV*—*XVIII*, *XX* and *XXI*, the structures of which were proposed on the basis of PMR spectroscopy. The products derived from cholestane (*VII*—*XI*) are a minority. This result is interpreted as a consequence of the small ability of chlorine to form epihalonium ions.

In our previous paper[1] we indicated that the reaction of 5,6β-dibromo-5α-cholestan-3β-ol (*I*) with silver fluoride is initiated predominantly by $C_{(5)}$-Br ionization and that it takes place predominantly *via* the stage of the carbonium and epibromonium ion *II* and *III*. In view of the fact that the transformation initiated by the $C_{(6)}$-Br ionization competes with this reaction to a certain extent, we considered it useful to study the behaviour of the analogous 5-bromo-6β-chloro derivative *IV* (ref.[2]) which under similar conditions reacted exclusively *via* the onium species *V* and *VI*. On reaction of an aqueous solution of silver perchlorate with a solution of chlorobromide *IV* in tetrahydrofuran we obtained a mixture of products from which we isolated halogen-free substances by chromatography on silica gel. We determined their structures on the basis of comparison with authentic samples as 4-cholesten-3-one (*VII*), 5-cholesten-3-one (*VIII*), 5-cholestene-3β,4β-diol (*IX*), 4-cholestene-3β,6β-diol (*X*) and 5α-cholestane-3β,5,6β-triol (*XI*). A further known component of the reaction mixture was 6β-chloro-5-methyl-19-nor-5β-cholest-9-en-3β-ol (*XII*) the structure of which we proved by conversion to authentic[3] acetate *XIII*. Benzoylation of the fraction containing 4-cholestenone gave in addition to unchanged 4-cholestenone four chloro derivatives of the composition $C_{34}H_{49}ClO_2$ (mass spectrometry). The strongly positive molecular rotations of these isomers, as well as the equatorial character of the 3α-proton and the axial character of the 6α-proton in the PMR spectra of these substances are typical properties of the products of Westphalen and backbone rearrangements. Only one of these isomers contains an olefinic proton (PMR: 5·45 p.p.m., bt, 1 H) and hence a trisubstituted double bond. On the basis

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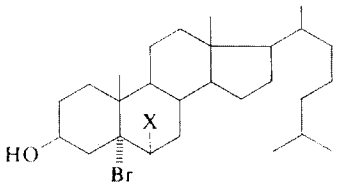
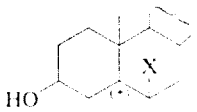
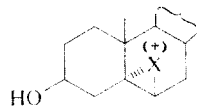
of analogy with the results of the related reaction[4-7] we proposed the structure of $\Delta^{1(10)}$-olefin *XV*. The less polar isomer *XVI* was submitted to oxidative degradation according to Castells and Meakins[8] and thus a product was obtained in the IR spectrum of which we detected absorption bands of a cyclopentanone system; hence, we assigned the substance *XVI* the structure of a $\Delta^{8(14)}$-olefin. The more polar isomer *XVII* displays in its PMR spectrum (Table I) the signal of a $C_{(6\alpha)}$ proton at the lowest field in this series, which may be explained by the deshielding effect of the tetrasubstituted double bond in its proximity, and hence, we assigned this substance the structure of a Δ^8-olefin. The most polar one of the isomeric chloro derivatives, *XVIII*, displays



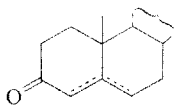
I, X = Br
IV, X = Cl



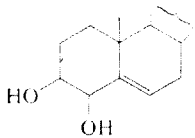
II, X = Br
V, X = Cl



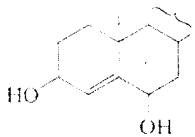
III, X = Br
VI, X = Cl



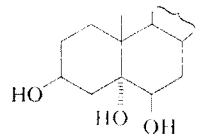
VII, Δ^4—C=C
VIII, Δ^5—C—C



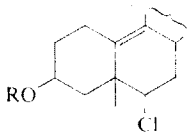
IX



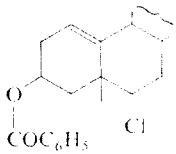
X



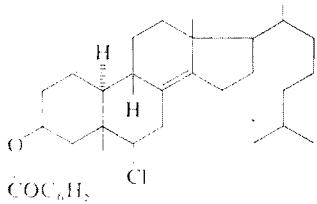
XI



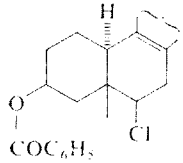
XII, R = H
XIII, R = Ac
XIV, R = C_6H_5CO



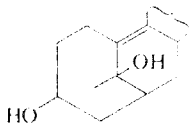
XV



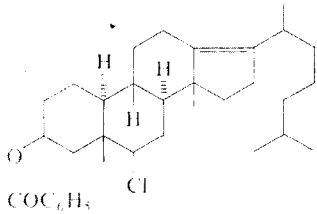
XVI



XVII



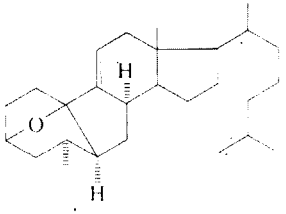
XX



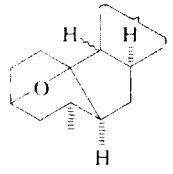
XVIII
XIX, 13,17-epoxide

in the PMR spectrum a downfield shift of the signal of $C_{(20)}$-proton to 2·41 p.p.m. (proved by a decoupling experiment), which indicates[7,9] that it is allylic with respect to the $\Delta^{13(17)}$-double bond; hence, we assigned the substance *XVIII* the structure of the product of backbone rearrangement.

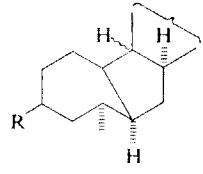
From the reaction mixture we also isolated a more polar substance than diol *X*; however, in its PMR spectrum this substance appears as a complex mixture. The same mixture (according to IR spectra) was obtained on treatment of the mixture of chloro derivative *XII* and its isomers with the reagent used, and therefore this mixture can be classified without further study among the products of rearrangement of the cholestane skeleton. Diol *XX*, formulated according to the analogy with the results of a related reaction, *i.e.* solvolysis of 6β-methanesulfonyloxy-5β-methyl-19-norcholest-9-ene[10], may represent the principal component of this mixture.



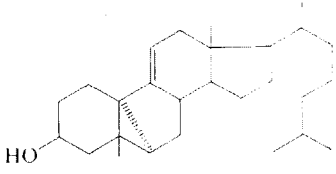
XXI



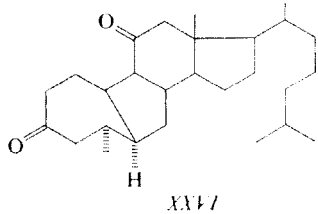
XXII



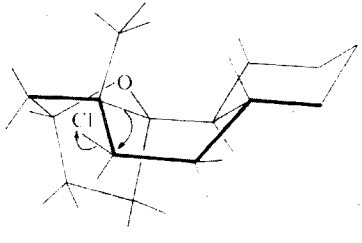
XXIII, R = OH
XXIV, R = O



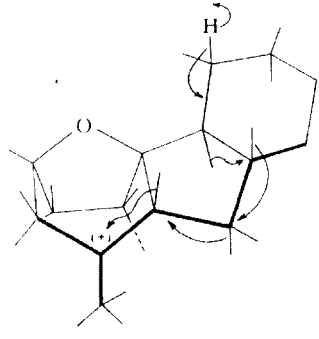
XXVIII



XXVI



XXVII



XXIX

A further product was oxido derivative *XXI* of the composition $C_{27}H_{46}O$ (mass spectrometry). Its PMR spectrum indicates a signal of a single —CH—O— proton (4·48 p.p.m.) and an olefinic proton (5·02 p.p.m.). The signal of the $C_{(19)}$-protons appears as a doublet at 0·92 p.p.m. Catalytic hydrogenation of this compound affords a mixture of dihydro derivative *XXII* and tetrahydro derivative *XXIII* the PMR spectra of which are similar to that of the starting oxide, with the exception of the olefinic signals, which disappeared. The IR spectra of compounds *XXI* to *XXIII* show that in the first two cases the substances are oxides, and the third is a hydroxy derivative. Oxidation of tetrahydro derivative *XXIII* according to Jones gave ketone *XXIV* with the oxo group in a seven-membered ring, and we therefore formulate the structures *XXI* to *XXIV* as derivatives of A-homo-B-norcholestane. The fact that we were also able to prepare hydroxy derivative *XXIII* from 6β-chloro-5-methyl-19-nor-5β-cholest-9-en-3β-ol (*XII*) by hydrogenolysis with lithium aluminum hydride[10] and catalytic hydrogenation shows that the 19-methyl group is not located on carbon $C_{(10)}$, but on $C_{(5)}$. The localisation of the double bond in oxide *XXI* in the six-membered ring C is based on the results of hydroboration and oxidation, during which we obtained in addition to a not quite identified boric acid derivative *XXV* also diketone *XXVI* in the IR spectrum of which there were frequencies of a cyclohexanone and a cycloheptanone system.

The formation of oxide *XXI* may be explained in two ways; the first supposes an interaction of the 3β-hydroxy group with the carbonium ion formed in the position $C_{(10)}$ and a subsequent transformation of the chloro oxide *XXVII* thus formed. The second supposes the participation of the double bond in the solvolysis of chlorine in the product of Westphalen rearrangement (*XII*) which could[10] afford a cyclopropane derivative, *XXVIII*, the isomerization of which would lead to oxide *XXI*. However, in a model experiment the transformation of chloro derivative *XII* did not give any oxide *XXI*, which excludes the second and indirectly supports the first of the mentioned hypotheses. The absolute configuration (5β, 6α, 8α) is assigned to single centres in compound *XXI* on the basis of the assumed sequence (Scheme 1) which is initiated by solvolysis of the $C_{(6\beta)}$—Cl bond, followed by migration of the $C_{(10)}$—$C_{(5)}$ bond with inversion at carbon $C_{(6)}$. The carbonium intermediate *XXIX* then undergoes a series of 1,2-hydride shifts, which is terminated by the formation of a double bond in the position 9(11).

To summarize it may be said that the solvolysis of 6β-chloro derivatives *IV*, catalysed with silver ions, takes place – in contrast[1] to the transformation of bromo derivative *I* – predominantly with the rearrangement of the methyl group from carbon $C_{(10)}$ to carbon $C_{(5)}$, under formation of the products of Westphalen's and backbone rearrangements. A higher yield of Wagner–Meerwein rearrangement in derivatives with the more electronegative chlorine in position 6β is in accordance with the results of Blunt and coworkers[11] who found a dependence between the degree of the re-

arrangement and the electronegativity of the 6β-substituent in compounds generating $C_{(5)}$-carbonium ion. As the stability of epihalonium ions is in similar dependence on the electronegativity of the corresponding halogen[12], we consider the higher yield of migration in chloro derivative *IV* a consequence of the fact that the equilibrium between the onium species[13] *V* and *VI* is shifted more to the left than in the case of ions *II* and *III*, and, hence, that in the mentioned chloro derivative *IV* higher effective concentration of the carbonium ion is attained in which 1,3-diaxial non-bonding interactions between the substituents in the positions 6β and 4β, 8β, 10β persist.

EXPERIMENTAL

The melting points were determined on a Kofler block and they are not corrected. Samples for analysis were dried at room temperature and in a 0·2 Torr vacuum for 8 hours, over phosphorus pentoxide. The infrared spectra were measured in tetrachloromethane unless otherwise stated. The ultraviolet spectra were measured in ethanol, circular dichroism and specific rotations in chloroform. The PMR spectra were measured in deuteriochloroform on a Varian HA-100 (100 MHz) instrument and the data are summarized in Table I. The identity of samples obtained by various routes were proved by comparison of their infrared spectra and on the basis of mixture melting points.

Reaction of 5-Bromo-6β-chloro-5α-cholestan-3β-ol *IV* with an Aqueous Silver Perchlorate Solution

A solution of 400 mg of compound *IV* in 2·5 ml of tetrahydrofuran was added under nitrogen to a solution of 0·5 ml of 40% aqueous silver perchlorate and the mixture was stirred in darkness for 18 hours. After dilution with 50 ml of chloroform the mixture was decanted from the precipitate which was washed with two 25 portions of chloroform. The combined chloroform extracts were washed with water, dried over sodium sulfate and evaporated *in vacuo*. The residue was applied on a thin-layer plate in dichloromethane solution and chromatographed twice with 10% of ether in benzene solution. Detection was carried out by spraying the plates with 0·2% morine in methanol and inspection under UV light. Elution of zones with ethyl acetate gave the following substances in sequence of increasing polarity: *1)* Mixture of hydrocarbons (8 mg) of unknown structure, $C_{27}H_{42}$, complex absorption in the UV region. On standing in air these substances are converted rapidly to mixtures of peroxides. *2)* 3β,10-Oxido-5α-methyl-A-homo-19,B-dinor-6α,8α-cholest-9(11)-ene (*XXI*), 21 mg, m.p. 137–138°C (methanol), $[\alpha]_D^{20}$ +17° (*c* 1·3); IR spectrum: 3025, 1015, 955 and 907 cm^{-1}, mass spectrum: M^+/e 384. For $C_{27}H_{44}O$ (384·6) calculated: 84·31% C, 11·53% H; found: 84·33% C, 11·57% H. *3)* Cholestenone fraction (90 mg), see Acetylation and benzoylation of cholestenone fraction); *4)* 3β,4β-dihydroxy-5-cholestene (*IX*), 57 mg after rechromatography in benzene–ether 1 : 1, m.p. 176–177°C (dichloromethane, heptane), $[\alpha]_D^{21}$ −62° (*c* 0·8); *5)* 3β,6β-dihydroxy-4-cholestene (*X*), 24 mg after rechromatography, m.p. 254–260°C (benzene), $[\alpha]_D^{21}$ +10° (*c* 0·5); *6)* a mixture containing probably substance *XX* (110 mg after rechromatography), IR spectrum: 3600, 3420 cm^{-1}. M^+/e 402. *7)* 5α-Cholestane-3β,5,6β-triol (*XI*), 39 mg, m.p. 240–244°C, for $3_{27}H_{48}O_3$ (420·7) calculated: 77·09% C, 11·50% H; found: 76·90% C, 11·71% H.

Acetylation of cholestenone fraction: A solution of 90 mg of the fraction in 1 ml of pyridine was mixed with 1 ml of acetic anhydride and allowed to stand overnight at room temperature. Methanol (2 ml) was added to the mixture and after two hour's standing the mixture was evaporated in a vacuum. The residue was chromatographed on a thin layer of silica gel with 5% of ether

in benzene mixture. Detection was carried out under UV light after spraying with morine. Elution with ether gave the following, consecutive fractions: 3β-acetoxy-6β-chloro-5-methyl-19-nor-5β-cholest-9-ene[3] (*XIII*), 20 mg, m.p. 134–136°C (ethanol), $[\alpha]_D^{20}$ +131° (*c* 1·0); IR spectrum: 1 739, 1 243 and 1 019 cm^{-1}; a mixture of acetates, 39 mg; 5-cholesten-3-one (*VIII*), 21 mg, m.p. 80–82°C, IR spectrum: 1 680 and 1 620 cm^{-1}.

Benzoylation of Cholestenone Fraction

The cholestenone fraction (3·1 g) obtained from 8·7 of chlorobromide *IV* as above was benzoylated in 15 ml of pyridine with 6 ml of benzoyl chloride at room temperature. The mixture was decomposed by pouring it onto ice, acidified with dilute hydrochloric acid. It was then extracted

TABLE I

Proton Magnetic Resonance Data of 5-Methylcholestane Derivatives

The spectra were measured in $CDCl_3$ with tetramethylsilane as internal reference on a Varian HA-100 (100 MHz) instrument. Chemical shifts are given in δ-units (p.p.m.) and the coupling constants in Hz.

Compound	$C_{(3)}$—H[a]	$C_{(6)}$—H ($J_{6,7\beta}$; $J_{6,7\alpha}$)	$C_{(5)}$—CH_3[b]	$C_{(13)}$—CH_3[c]	$C_{(20)}$—CH_3[d]	$C_{(25)}(-CH_3)_2$[d]
XIV[e]	5·37	4·04 (12; 4)	1·36	0·81	0·90	0·87
XV[f]	5·45	4·07 (9; 9)	1·37	0·65	0·91	0·87
XVI[g]	5·38	3·63 (12; 4·5)	1·30	0·86	0·94	0·88
XVII[h]	5·46	4·74 (12; 4·5)	1·21	0·66	0·91	0·87
XVIII[i]	5·37	3·78 (9; 7)	1·23	—	0·96	0·84
XIX[j]	5·37	3·81 (10; 6)	1·23	—	1·04	0·86
XXI[k]	4·48	1	0·92	0·65	0·92	0·86
XXII	4·25	1	0·89	0·65	0·91	0·86
XXIII	3·90	1	0·89	0·65	0·91	0·86
XXIV	—	1	0·94	0·64	0·91	0·86

[a] Multiplet with W = 12–15 Hz for *XIV*–*XIX* and W = 25 Hz for *XXI*–*XXIV*; [b] singlet in the case of 5β-methyl derivatives *XIV*–*XIX* and a doublet with *J* = 6·5 Hz in the case of 5α-methyl derivatives *XXI*–*XXIV*; [c] singlet; [d] doublet with *J* = 6·0–6·5 Hz; [e] 7·30–7·60 m, 3 H; 7·95 to 8·15 m, 2 H (—C_6H_5); [f] 7·30–7·65 m, 3 H; 7·95–8·15 m, 2 H (—C_6H_5) 5·45 m, 1 H ($C_{(1)}$—H; overlap with $C_{(3)}$—H); [g] 7·30–7·70 m, 3 H; 7·95–8·15 m, 2 H (—C_6H_5); [h] 7·30–7·60 m, 3 H; 8·05–8·25 m, 2 H (—C_6H_5); [i] 7·30–7·60 m, 3 H; 7·95–8, 15 m, 2 H, (—C_6H_5); 0·93 s, 3 H ($C_{(14)}$—CH_3); 2·41 m ($C_{(21)}$—H); [j] 7·30–7·60 m, 3 H; 7·95–8·15 m, 2 H (—C_6H_5); 0·91 s, 3 H ($C_{(14)}$—CH_3); [k] 5·02 bt, 1 H ($C_{(11)}$—H); [l] indeterminable values — the signal is overlapped in the steroid envelope.

with light petroleum. After washing of the extract with dilute hydrochloric acid, water, a potassium hydrogen carbonate solution, and water, the mixture was dried over sodium sulfate and concentrated *in vacuo*. The residue was introduced onto a column of 150 g of silica gel and the column eluted with 10% of benzene in light petroleum mixture. The substances were obtained in the following order: 3β-Benzoyloxy-6β-chloro-5-methyl-19-nor-5β-cholest-9-ene (*XIV*), 877 mg, m.p. 151–153°C (ethanol), $[\alpha]_D^{20}$ +148° (*c* 1·3); IR spectrum: 1719 and 1274 cm^{-1}; for $C_{34}H_{49}ClO_2$ (525·2) calculated: 77·75% C, 9·40% H; found: 77·79% C, 9·38% H. 3β-Benzoyloxy-6β-chloro-5-methyl-19-nor-5β,9β,10α-cholest-8(14)-ene (*XVI*), 113 mg; $[\alpha]_D^{20}$ +95° (*c* 0·9); for $C_{34}H_{49}ClO_2$ (525·2) calculated: 77·75% C, 9·40% H; found: 77·48% C, 9·63% H. 3β-Benzoyloxy-6β-chloro-5-methyl-19-nor-5β-cholest-1(10)-ene (*XV*), 204 mg, $[\alpha]_D^{20}$ +44° (*c* 0·9); for $C_{34}H_{49}ClO_2$ (525·2) calculated: 77·75% C, 9·40% H; found: 77·50% C, 9·66% H. 3β-Benzoyloxy-6β-chloro-5-methyl-19-nor-5β,10α-cholest-8-ene (*XVII*), 430 mg, m.p. 170–172°C, $[\alpha]_D^{20}$ +64° (*c* 1·1); IR spectrum: 1719 and 1279 cm^{-1}; for $C_{34}H_{49}ClO_2$ (525·2) calculated: 77·75% C, 9·40% H; found: 77·81% C, 9·43% H. 3β-Benzoyloxy-6β-chloro-5,14-dimethyl-18,19-dinor-5β,8α,9β,10α,14β-cholest-13(17)-ene (*XVIII*), 895 mg, m.p. 48–51°C, $[\alpha]_D^{20}$ +52° (*c* 0·9); IR spectrum: 1720, 1274, 1604, 1586 and 1493 cm^{-1}; for $C_{34}H_{49}ClO_2$ (525·2) calculated: 77·75% C, 9·40% H; found: 77·52% C, 9·18% H.

3β-Benzoyloxy-6β-chloro-5,14-dimethyl-13,17-oxido-18,19-dinor-5β,8α,9β,10α,13α,14β-cholestane (*XIX*)

a) Perphthalic acid (75 mg) in 1 ml of ether was added to a solution of 100 mg of substance *XVIII* in 1 ml of ether and the mixture was allowed to stand at room temperature for 18 hours. The separated phthalic acid was filtered off under suction, washed with ether and the combined ethereal filtrates were washed with aqueous potassium hydrogen carbonate solution and water. After drying over sodium sulfate and evaporation, the product was crystallized from methanol, m.p. 167–169°C (65 mg); $[\alpha]_D^{20}$ +53° (*c* 0·8). IR spectrum: 1721, 1603, 1586 and 1272 cm^{-1}. For $C_{34}H_{49}ClO_3$ (541·2) calculated: 75·45% C, 9·13% H; found: 75·44% C, 9·20% H.

b) The intermediate fraction (160 mg) containing compounds *XVII* and *XVIII* was oxidized with perphthalic acid under the above conditions. After working up 86 mg of epoxide *XIX*, 5 mg of another epoxide, and 50 mg of unreacted substance *XVII* were isolated.

Reaction of 5-Bromo-6β-chloro-5α-cholestan-3β-ol with Silver Tetrafluoroborate

Substance *IV* (300 mg) in 3 ml of benzene was added under stirring to a solution of silver tetrafluoroborate (250 mg) in 10 ml of benzene and the mixture was shaken after 20 minutes' reaction with 5 ml of a saturated aqueous sodium chloride solution. The mixture was diluted with benzene and centrifuged. The organic layers were separated, washed with water, dried over sodium sulfate and evaporated *in vacuo*. Chromatography on a silica gel column (25 g) with benzene gave 51 mg of hydrocarbon $C_{27}H_{46}$, 11 mg of 3β,10-oxido derivative *XXI*, 110 mg of cholestenone fraction, and 36 mg of a mixture of dihalogenocholestan-3β-ols (mass spectrum: presence of F, Cl and Br). Benzoylation of the cholestenone fraction gave, after thin layer chromatography, 9 mg of 4-cholestenone (*VII*) and 89 mg of 3β-benzoyloxy-6β-chloro-5,14-dimethyl-18,19-dinor5β,8α 9β,10α,14β-cholest-13(17)-ene (*XVIII*).

Oxidation of $\Delta^{8(14)}$-Double Bond in Substance *XVI*

18 mg of osmium tetroxide in 2 ml of tetrahydrofuran were added to a solution of 16 mg of compound *XVI* in 2 ml of tetrahydrofuran and the mixture allowed to stand at 37°C for 7 days.

It was then refluxed with lithium aluminum hydride in tetrahydrofuran for 30 minutes and additioned with a saturated aqueous sodium sulfate solution. The mixture was filtered through a small column of sodium sulfate and the filtrate evaporated. The solution of the product in 1 ml of benzene and 2 ml of acetic acid was mixed with 40 mg of lead tetra-acetate and allowed to react for one week. After dilution with benzene and filtration through a silica gel column the filtrate was evaporated to dryness. The residue was then dissolved in 0·5 ml of chloroform and 1 ml of methanol and hydrolysed with 3 drops of hydrochloric acid at 37°C for 20 hours. After dilution with chloroform and washing with an aqueous potassium hydrogen carbonate solution and water the mixture was filtered through sodium sulfate. The IR spectrum of the product shows absorption at 1731 cm^{-1} (ν(C=O) in a five-membered ring).

5-Cholesten-3-one (*VIII*)

A solution of 100 mg of substance *IV* in 1 ml of tetrahydrofuran was allowed to react with 0·1 ml of a 50% aqueous solution of silver perchlorate for 30 minutes. Chromatography of the products on a silica gel thin-layer plate gave 6 mg of a substance of R_F 0·50 (in benzene) the infrared spectrum of which was identical with the spectrum of 5-cholesten-3-one (*VIII*).

Reaction of 3β-Hydroxy-6β-chloro-5-methyl-19-nor-5β-cholest-9-ene with Silver Perchlorate

A solution of 76 mg of compound *XII* in 3 ml of tetrahydrofuran was stirred with 0·15 ml of an aqueous silver perchlorate solution (50%) for 3 hours under nitrogen. Thin-layer chromatography showed that a complete transformation of compound *XII* took place, but oxide *XXI* was not present in the mixture in a detectable amount. The main product of reaction (46 mg) which on spraying with sulfuric acid gave a yellow spot, was isolated by preparative thin-layer chromatography (in ether between substances *X* and *XI*). The infrared spectrum of this compound is identical with that of the main polar product of transformation of compound *IV*.

3β,10-Oxido-5β-methyl-A-homo-19,B-dinor-6α,8α,9ξ-cholestane (*XXII*)

A solution of 220 mg of compound *XXI* in acetic acid was hydrogenated on 200 mg of platinum catalyst for 5 hours. After filtration off of the catalyst the solution was evaporated. The residue was dissolved in light petroleum and put on a silica gel column. Chromatography with 20% of benzene in light petroleum gave 97 mg of the main product, m.p. 56—58°C (ethanol), $[\alpha]_D^{20}$ +23° (*c* 1·2), M^+/e 386; IR spectrum: 1035, 1000, 962 and 939 cm^{-1}. For $C_{27}H_{46}O$ (386·6) calculated: 83·87% C, 11·99% H; found: 83·90% C, 11·82% H.

5α-Methyl-A-homo-19,B-dinor-6α,8α,9ξ,10ξ-cholestan-3β-ol (*XXIII*)

a) *From oxide* XXI: The last fractions from the preceding chromatography gave on elution with benzene 31 mg of compound *XXIII* of m.p. 133—135°C (heptane), $[\alpha]_D^{20}$ −30° (*c* 0·5); IR spectrum: 3620 and 1038 cm^{-1}. For $C_{27}H_{48}O$ (388·6) calculated: 83·43% C, 12·45% H; found: 83·30% C, 12·65% H.

b) *From acetate* XIII: A solution of 130 mg of acetate *XIII* in 5 ml of tetrahydrofuran was added dropwise over 5 minutes and under nitrogen to a boiling solution of 400 mg of lithium aluminum hydride in 10 ml of tetrahydrofuran, and the mixture was refluxed for 4 hours. After cooling the mixture was decomposed by addition of aqueous sodium sulfate and then saturated with solid sodium sulfate and filtered through a layer of sodium sulfate. The residue of the filtrate was dissolved in 5 ml of acetic acid and hydrogenated on 30 mg of platinum oxide. The hydrogena-

tion product was chromatographed on a column of 10 g of silica gel with benzene. A substance was isolated which had the same polarity as hydroxy derivative *XXIII* (11 mg), m.p. 126–129°C and 133–135°C (methanol), undepressed on admixture with the sample prepared uder *a*).

5α-Methyl-A-homo-19,B-dinor-6α,8α,9ξ,10ξ-cholestan-3-one (*XXIV*)

Hydroxy derivative *XXIII* (20 mg) was oxidized in acetone according to Jones to give 20 mg of product which after purification by thin-layer chromatography (with 8% of ether in benzene) gave 16 mg of ketone *XXIV*, m.p. 93–94°C (acetone, at −60°C); $[\alpha]_D^{20}$ +20° (*c* 0·9), Δε (291 nm) +3·08, IR spectrum: 1705 cm. For $C_{27}H_{46}O$ (386·6) calculated: 83·87% C, 11·99% H; found: 83·71% C, 11·95% H.

Hydroboration of Oxide *XXI*

A mixture of diborane and nitrogen was introduced under nitrogen into a solution of 40 mg of substance *XXI* in 3 ml of dioxan. After 20 minutes the solution was evaporated and the residue oxidized with Jones' reagent in acetone. The product was isolated by pouring the solution into a solution of potassium hydrogen carbonate and extraction with benzene. The concentrated benzene solution was filtered through a layer of sodium sulfate (removal of boric acid), concentrated and applied onto a preparative thin-layer plate with silica gel (development with 10% ether in benzene, detection with morin). Elution of the zone with R_F 0·1 with ether gave 20 mg of boric acid ester, m.p. 136–139°C; $[\alpha]_D^{20}$ +36° (*c* 0·4); M^+/e 416, 386; IR spectrum: 3650, 3630, 1378 and 1335 cm^{-1}. Elution of the band of R_F 0·55 with ether gave 5 mg of diketone *XXVI*, m.p. of the crude product was 115–119°C; IR spectrum: 1702 and 1725 cm^{-1}; M^+/e 400, Δε (302 nm) +1·93.

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