TRANSANNULAR PARTICIPATION OF THE HYDROXYL GROUP IN WOODWARD ADDITION TO SOME 5-HYDROXY-5α-CHOLEST-2-ENES*

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By the application of Woodward addition to some 5-hydroxy-5α-cholest-2-enes (*Ia—Id*) two types of products (*IIa—IId* and *IIIa—IIId*) were obtained. The mechanism of their formation is discussed.

As part of a program aimed at preparation of Westphalen-type steroids, a route to 2β,3β,5-trihydroxy-5α-cholestanes with or without an oxygen function at position 6 was sought. In the preceding paper[1] we reported on the preparation of substituted 2-cholestenes *Ia—Id* that we considered to be promissing starting compounds for the preparation of the desired triols. To this end, we investigated the application of the Woodward hydroxylation reaction[2] which has been generally used in recent years for its simplicity, reliability and good yields. It was also successfully applied to a variety of 2-cholestenes in the syntheses of ecdysones and their analogues.

When we applied this reaction to 2-cholestenes *Ia—Id*, we always obtained pairs of products *IIa—IId* and *IIIa—IIId* after acetylation of the crude reaction product. Whereas type *III* corresponds to normal reaction, formation of the cyclic ethers of type *II* is due to participation of the 5α-hydroxyl. In our experiments, the mutual proportion of both types varied considerably depending on the nature and configuration of the substituent at position 6 (Table I). In the instance of 6-unsubstituted

TABLE I

Yields and Ratios of Products of Woodward Addition

Starting compound	*Ia*	*Ib*	*Ic*	*Id*
Total yield, %	96	97	94	97
Ratio *II* : *III*	62 : 38	32 : 68	48 : 52	61 : 39

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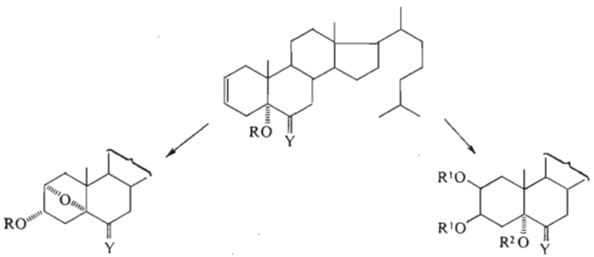
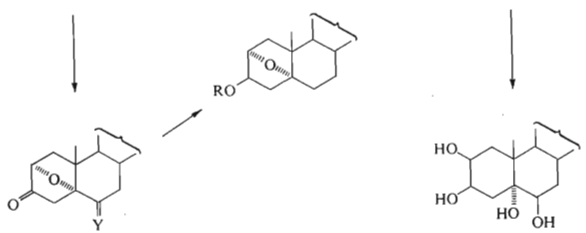
(*Ia*) and 6α-substituted (*Id*) 2-cholestenes the ratio of cyclized to normal products is approximately 1 : 1. In the instance of the 6-oxo derivative *Ib*, participation of the 5-hydroxyl is largely suppressed and the simple addition product *IIIb* strongly



IIa, R = Ac, Y = H_2
IIb, R = Ac, Y = O
IIc, R = Ac, Y = OBz / H
IId, R = Ac, Y = H / OBz
IIe, R = Ac, Y = OAc / H
IIf, R = H, Y = H_2
IIg, R = H, Y = O
IIh, R = H, Y = OH / H
IIi, R = Mes, Y = H_2
IIj, R = Mes, Y = O

Ia, R = H, Y = H_2
Ib, R = H, Y = O
Ic, R = H, Y = OBz / H
Id, R = H, Y = H / OBz
Ie, R = Ac, Y = O

IIIa, R^1 = Ac, R^2 = H, Y = H_2
IIIb, R^1 = Ac, R^2 = H, Y = O
IIIc, R^1 = Ac, R^2 = H, Y = OBz / H
IIId, R^1 = Ac, R^2 = H, Y = H / OBz
IIIe, R^1 = Ac, R^2 = Ac, Y = O
IIIf, R^1 = Ac, R^2 = Ac, Y = H_2
IIIg, R^1 = Ac, R^2 = Ac, Y = OBz / H
IIIh, R^1 = H, R^2 = H, Y = O
IIIi, R^1 = Bz, R^2 = H, Y = O



IVa, Y = H_2
IVb, Y = O

V, R = H
VI, R = Mes

VII

prevails over the cyclic ether *IIb*. The normal reaction course can be ensured by acetylation of the 5α-hydroxy group in the starting compound. Thus, Woodward addition to the 5α-acetoxy derivative *Ie* resulted in the exclusive formation of *IIIe* that proved to be identical with the substance prepared from 5α-hydroxy derivative *IIIb* on acetylation.

TABLE II

^{1}H-NMR Data of 2α,5α-Epoxides

Compound (ref.)	18-H	19-H	2β-H ($J_{2\beta,1\alpha}$)	3-H ($J_{3\beta,4\beta}$, $J_{3\beta,4\alpha}$)
IIa (3)	0·68	0·92	4·34 d (6·0)	4·71 dd (7·0, 3·0)
IIb	0·67	0·94	4·59 d (6·2)	4·62 dd (6·8, 2·8)
IIc	0·70	1·23	4·45 d (6·6)	4·76 dd (6·8, 2·4)
IId	0·70	1·04	4·51 d (6·2)	4·76 dd (7·0, 2·4)
IIe (5)	0·70	1·06	4·40 d (6·0)	4·73 dd (7·0, 2·6)
IIf	0·68	0·90	4·28 d (6·0)	3·81 dd (6·0, 2·5)
IIg	0·66	0·90	4·44 d (6·5)	3·83 dd (6·5, 2·0)
IIh	0·69	1·03	4·21 d (7·0)	3·86 dd (7·0, 2·0)
IIi (3)	0·68	0·91	4·53 d (6·0)	4·77 d (7·0, 3·0)
IIj	0·66	0·90	4·79 d (6·6)	4·77 dd (6·6, 4·2)
IVa (4)	0·69	1·01	4·28 d (7·0)	—
IVb	0·69	1·08	4·52 d (6·6)	—
V (4)	0·68	1·04	4·28 m	4·28 m
VI (4)	0·67	1·02	4·50 m	4·90 m

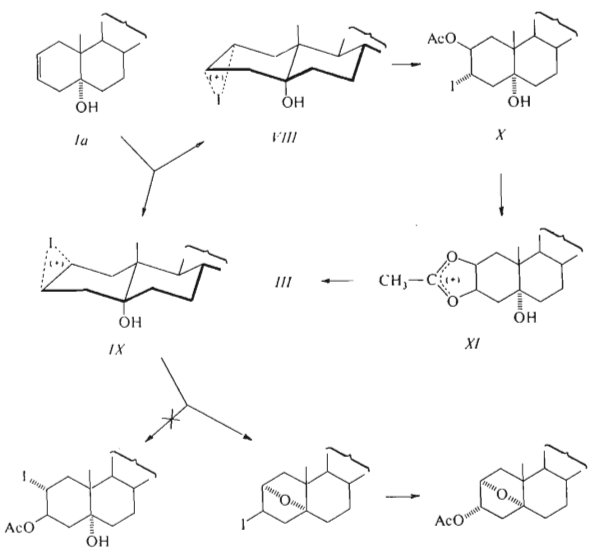
Proof of the structure of cyclic ethers is based on the identity of the ether *IIa* with a compound prepared in a different manner[3,4]. Similarly, chemical correlation proved the structure of the benzoate *IIc*, that was converted *via* the diol *IIh* into the known[5] diacetate *IIe*. An attempt at correlating the 6-oxo derivative *IIb* with *IIa* or *IIf* by removing its oxo group was unsuccessful since both Huang-Minlon reduction and tosylhydrazone reduction with cyano borohydride led to complicated mixtures containing no *IIa* or *IIf*. The position of the substituents in *IIb* was established by conversion of the latter compound to the diketone *IVb* (*via* the alcohol *IIg*) that was also obtained from the diol *IIh*. Comparison of the ^{1}H-NMR spectra of the compound *IIa* with the spectra of *IIb*–*IId* (Table II) reveals identity in relevant spectroscopic features due to A-ring protons at $C_{(2)}$ and $C_{(3)}$. The signal of 2β-proton appears in the 4·3–4·6 ppm region as a broad doublet with $J_{2\beta,1\alpha} = 6$ Hz the coupling constants with other neighboring protons being negligible. The signal of the 3β-proton appears at 4·6–4·8 ppm as a doublet of doublets and coupling constants $J_{3\beta,2\beta} = 0$ Hz, $J_{3\beta,4\beta} = 7$ Hz and $J_{3\beta,4\alpha} = 3$ Hz. The shape of the signals in all compounds (*IIa*–*IId*) is identical, small differences in chemical shifts are due to the character of the 6-substituent. This constitutes additional and complementary evidence for the structures of cyclic ethers.

For the products of simple addition, the structure of 2β,3β-disubstituted cholestanes may be assumed from analogy. Indeed, ^{1}H-NMR spectroscopy shows the presence of one axial and one equatorial acetoxy group in each of the compound *IIIa*–*IIId* (Table III). The positive sign of the Cotton effect at 236 nm in dibenzoate *IIIi* is only compatible with the axial-equatorial relationship[6]. Direct structure proof is given by the conversion of *IIIb* and *IIIc* into a known[7] tetraol *VII* by reduction with lithium aluminum hydride.

TABLE III
^{1}H-NMR Data of 2,3-Diacetates

Compound	18-H	19-H	2α-H	3α-H
IIIb	0·65	1·12	5·37 m	5·37 m
IIIc	0·64	0·96	5·49 m	5·45 m
IIId	0·68	1·41	5·37 m	5·40 m
IIIa	0·68	1·25	5·50 m	5·50 m
IIIe	0·65	1·03	5·34 d	5·00 m
IIIf	0·66	1·16	5·38 m	5·00 m
IIIg	0·70	1·51	5·38 m	4·89 m
IIIi	0·65	1·14	5·73 m	5·58 m

One interesting feature of the above reaction should be pointed out: Both 2α,3α- and 2β,3β-iodonium ions *VIII* and *IX* are involved in the reaction. Formation of the 2α,3α-iodonium ion *VIII* must be assumed in the normal reaction leading (after acetylation) to 2β,3β-diacetate *III*. 2β,3β-Iodonium ion *IX* should be an intermediary species in the formation of 2α,5α-epoxides *II* (*cf.* Scheme 1). Since no



SCHEME 1

2α,3α-diacetate could be isolated, either the concentration of the 2β,3β-iodonium ions in the equilibrium between *I*, *VIII* and *IX* is small or the rate of the acetolysis of 2β,3β-iodonium ions is slow as compared with that of the 2α,3α-epimer. In any case, formation of 2α,5α-epoxide *II* from 2β,3β-iodonium ion *IX* may successfully compete with the acetolysis of the 2α,3α-iodonium ion if the attack of the 5α-hydroxyl at $C_{(2)}$ is a relatively fast reaction. This is likely to be the case for steric arrangement of the respective reaction centers in *IX* favoring this intramolecular reaction.

EXPERIMENTAL

Melting points were determined on a Kofler block. Analytical samples were dried at 50°C/0·2 Torr. Optical measurements were carried out in chloroform with an error of ±1°. The infrared spectra were recorded on a Zeiss UR-20 spectrometer in tetrachloromethane unless stated otherwise. The ^{1}H-NMR spectra were recorded on a Varian HA-100 instrument in deuteriochloroform with tetramethylsilane as internal reference at 30°C. Chemical shifts are given in ppm. Apparent coupling constants were obtained from the first order analysis. The mass spectra were recorded on a AEI MS 907 mass spectrometer. The CD spectra were recorded on a Dichrograph II (Jouan--Roussel) in methanol. The identity of samples prepared by different routes was checked by mixture melting point determination, by thin-layer chromatography (TLC) and by infrared and ^{1}H-NMR spectra. Usual work up of an ethereal solution means washing the solution with 5% aqueous hydrochloric acid, water, 5% aqueous potassium hydrogen carbonate solution, water, drying with sodium sulfate and evaporation of the solvent *in vacuo*.

Woodward Addition to 5α-Cholest-2-en-5-ols

A solution of iodine (260 mg, 2·0 mg-at) in tetrahydrofuran (2 ml) was added dropwise in the course of 30 min. to a stirred solution of olefin[1] (1 mmol) in glacial acetic acid (7 ml) and tetrahydrofuran (1 ml) containing silver acetate (370 mg, 2·2 mmol). Stirring was continued for an additional 30 min at room temperature and solution of water (20 mg, 1·1 mmol) in acetic acid (1 ml) was added, the temperature raised to 95°C and stirring continued for 3 h. The mixture was passed through a column of sodium chloride, washed with chloroform and the filtrate evaporated *in vacuo*. The residue was dried azeotropically with benzene and acetylated with acetic anhydride (1 ml) in pyridine (3 ml) at room temperature overnight. The mixture was decomposed with ice, the product taken up in ether and the ethereal solution worked up as usual. The residue was chromatographed on four preparative silica gel plates (20 × 20 cm) using double development with a mixture of benzene and ether (95 : 5) as eluent. The faster-moving substance was an epoxide (*IIa*—*IId*), the slower one was the product of normal addition (*IIIa*—*IIId*). The separated zones were detected with morin (0·2% solution in methanol), the substances were eluted with ether and the eluates were evaporated. The ratio of the products is given in Table I. Analytical and physical data of isolated compounds are given in Table IV.

2α,5-Epoxy-3α-acetoxy-5α-cholestan-6-one (*IIb*)

The alcohol *IIg* (20 mg) was acetylated with acetic anhydride (0·2 ml) in pyridine (1 ml) at room temperature for 8 h. The mixture was decomposed with ice, the product taken up in ether and the ethereal solution worked up as usual. The residue was crystallized from a mixture of acetone, methanol and water to yield the acetate *IIb* (11 mg), m.p. 86—87°C. For $C_{29}H_{46}O_4$ (458·7) calculated: 75·94% C, 10·11% H; found: 76·02% C, 10·18% H.

2α,5-Epoxy-5α-cholestane-3α,6β-diol 3,6-Diacetate (*IIe*)

The diol *IIh* (100 mg) was acetylated with acetic anhydride (1 ml) in pyridine (2 ml) at room temperature overnight. The mixture was worked up as given for *IIb* to yield the diacetate *IIe* (89 mg), m.p. 141—143°C (methanol), $[\alpha]_D^{20}$ —6° (*c* 1·7) in accordance with the literature[5].

2α,5-Epoxy-5α-cholestan-3α-ol (*IIf*)

The acetate *IIa* (90 mg) in ether (4 ml) was refluxed with lithium aluminum hydride (50 mg) for 10 min. The mixture was decomposed with saturated aqueous sodium sulfate solution, the product extracted with ether and the ethereal solution worked up as usual. The residue was crystallized from a mixture of acetone, methanol and water to afford the alcohol *IIf* (34 mg), m.p. 149–150°C, $[\alpha]_D^{20}$ +26° (*c* 1·8) in accordance with the literature[3]. IR spectrum: 3592, 3635 cm^{-1}.

2α,5-Epoxy-3α-hydroxy-5α-cholestan-6-one (*IIg*)

A solution of the acetate *IIb* (120 mg) and potassium hydroxide (100 mg) in methanol (7 ml) was refluxed for 1 h under nitrogen. Methanol was distilled off under reduced pressure, the residue was treated with ether and water, the organic layer was washed with water, dried and evaporated The residue was crystallized from a mixture of acetone and n-heptane to afford the alcohol *IIg* (62 mg), m.p. 150–151°C, $[\alpha]_D^{20}$ −13° (*c* 1·6). IR spectrum: 1718, 3594, 3630 cm^{-1}. For $C_{27}H_{44}O_3$ (416·6) calculated: 77·84% C, 10·64% H; found: 77·92% C, 10·61% H.

TABLE IV

Analytical and Physical Data of Products of Addition

Compound	Formula (m.w.)	Calculated/Found		M.p., °C $[\alpha]_D^{20}$
		% C	% H	
IIa	$C_{29}H_{48}O_3$	78·33	10·88	81–83[a]
	(444·7)	78·46	10·91	+18°
IIb	$C_{29}H_{46}O_4$	75·94	10·11	86–87
	(458·7)	76·12	10·08	−43°
IIc	$C_{36}H_{52}O_5$	76·56	9·28	oil
	(564·8)	76·48	9·25	−5°
IId	$C_{36}H_{52}O_5$	76·56	9·28	oil
	(564·8)	76·38	9·35	+44°
IIIa	$C_{31}H_{52}O_5$	74·77	10·38	145–146
	(504·8)	73·61	10·40	+23°
IIIb	$C_{31}H_{50}O_6$	71·78	9·72	182–183[b]
	(518·7)	71·69	9·63	−41°
IIIc	$C_{38}H_{56}O_7$	73·04	9·03	129–132
	(624·9)	73·19	8·99	−36°
IIId	$C_{38}H_{56}O_7$	73·04	9·03	211–212
	(624·9)	73·15	9·11	−45°

[a] In accordance with the literature[3]. [b] In accordance with the literature[9].

2α,5-Epoxy-5α-cholestane-3α,6β-diol (*IIh*)

The diester *IIc* (200 mg) in ether (10 ml) was refluxed with lithium aluminum hydride (100 mg) for 30 min. The mixture was worked up as given for *IIf*. The residue was crystallized from aqueous acetone to afford the diol *IIh* (43 mg), m.p. 205–206°C, $[\alpha]_D^{20}$ +2° (*c* 1·6). IR spectrum (chloroform): 3594, 3631 cm^{-1}. For $C_{27}H_{46}O_3$ (418·7) calculated: 77·46% C, 11·07% H; found: 77·32% C, 11·09% H.

2α,5-Epoxy-3α-methanesulfonyloxy-5α-cholestan-6-one (*IIj*)

The alcohol *IIg* (500 mg) in pyridine (5 ml) was treated with methanesulfonyl chloride (1 ml) at 0°C and allowed to stand at this temperature for 30 min. The mixture was decomposed with ice, the product taken up in ether, and the ethereal solution worked up as usual. The residue was crystallized from a mixture of acetone, methanol and water to yield the mesylate *IIj* (395 mg), m.p. 110–111°C, $[\alpha]_D^{20}$ −28° (*c* 1·9). For $C_{28}H_{46}O_5S$ (494·7) calculated: 67·98% C, 9·37% H, 6·48% S; found: 68·12% C, 9·33% H, 6·21% S.

2β,3β-Diacetoxy-5-hydroxy-5α-cholestan-6-one (*IIIb*)

The triol *IIIh* (100 mg) was acetylated with acetic anhydride (0·3 ml) in pyridine (1 ml) at room temperature overnight, the mixture was worked up as given for *IIb*. Crystallization of the residue from a mixture of acetone, methanol and water afforded the diacetate *IIIb* (42 mg), m.p. 181–182°C. For $C_{31}H_{50}O_6$ (518·7) calculated: 71·78% C, 9·72% H; found: 71·94% C, 9·76% H.

2β,3β,5-Triacetoxy-5α-cholestan-6-one (*IIIe*)

a) *From 5-acetoxy-5α-cholest-2-en-6-one*[1] (Ie): The Woodward addition to the olefin *Ie* (370 mg) was carried out as with *Ia–Id*. The crude reaction product was chromatographed on a column of silica gel (20 g) using light petroleum–ether (95 : 5) as eluent. Fractions containing the compound *IIIe* were collected, evaporated and the residue was crystallized from a mixture of acetone, methanol and water to yield the triacetate *IIIe* (293 mg), m.p. 134–135°C, $[\alpha]_D^{20}$ −5° (*c* 2·5). IR spectrum: 1245, 1739, 1751 cm^{-1}. For $C_{33}H_{52}O_7$ (560·8) calculated: 70·68% C, 9·35% H; found: 70·74% C, 9·29% H.

b) *From 2β,3β-diacetoxy-5-hydroxy-5α-cholestan-6-one* (IIIb): The alcohol *IIIb* (120 mg) was dissolved in acetic acid (4 ml) and acetylated with acetic anhydride (1 ml) in the presence of *p*-toluenesulfonic acid (50 mg) at room temperature for 2 h. The mixture was decomposed with ice, the product taken up in chloroform, the organic layer washed with 5% aqueous potassium hydrogen carbonate solution, water, dried and the solvent evaporated. The residue was crystallized from a mixture of acetone, methanol and water to yield the triacetate *IIIe* (47 mg), m.p. 133 to 134°C, identical with the product described under *a*).

5α-Cholestane-2β,3β,5-triol 2,3,5-Triacetate (*IIIf*)

The alcohol *IIIa* (90 mg) was dissolved in acetic acid (2 ml) and acetylated with acetic anhydride (0·5 ml) in the presence of *p*-toluenesulfonic acid (50 mg) at room temperature for 30 min. The mixture was decomposed with ice, the product taken up in chloroform, the organic layer washed with 5% aqueous potassium hydrogen carbonate solution, water, dried and the solvent evaporated. The residue was chromatographed on one preparative plate of silica gel (20 × 20 cm) using benzene–ether (95 : 5) as eluent. Corresponding zones were collected, eluted and evaporated

to yield the noncrystalline triacetate *IIIf* (59 mg). For $C_{33}H_{54}O_6$ (546·8) calculated: 72·49% C, 9·95% H; found: 72·39% C, 9·96% H.

5α-Cholestane-2β,3β,5,6β-tetraol 2,3,5-Triacetate 6-Benzoaze (*IIIg*)

The alcohol *IIIc* (60 mg) was dissolved in acetic acid (2 ml) and acetylated with acetic anhydride (0·5 ml) in the presence of *p*-toluenesulfonic acid (50 mg) for 4 h at room temperature. The mixture was worked up as given for *IIIf* to yield the noncrystalline triacetate *IIIg* (46 mg), $[\alpha]_D^{20}$ −29° (*c* 2·0). For $C_{40}H_{58}O_8$ (666·9) calculated: 72·04% C, 8·77% H; found: 72·06% C, 8·82% H.

2β,3β,5-Trihydroxy-5α-cholestan-6-one (*IIIh*)

a) *From* 2β,3β,5-*trihydroxy*-5α-*cholestan*-6-*one* 2,3-*diacetate* (IIIb): A solution of the diacetate *IIIb* (200 mg) in methanol (17 ml) was treated with a solution of potassium hydrogen carbonate (200 mg) in water (3 ml) and refluxed for 3 h. Methanol was distilled off under reduced pressure, the residue treated with ether and water, the organic layer washed with water, dried and evaporated. The residue was crystallized from aqueous acetone to yield the triol *IIIh* (32 mg), m.p. 291 to 293°C, $[\alpha]_D^{20}$ −22° (*c* 1·5). IR spectrum (KBr): 1713, 3330, 3450 cm^{-1}. For $C_{27}H_{46}O_4$ (434·7) calculated: 74·61% C, 10·67% H; found: 74·68% C, 10·72% H.

b) *From* 2β,3β,5-*triacetoxy*-5α-*cholestan*-6-*one* (IIIe): A solution of the triacetate *IIIe* (100 mg) and potassium hydroxide (100 mg) in methanol (10 ml) was refluxed for 2 h. Methanol was distilled off under reduced pressure, the residue treated with ether and water, the organic layer washed with water, dried and evaporated. The residue was crystallized from aqueous acetone to yield the triol *IIIh* (18 mg), m.p. 290−292°C.

2β,3β-Dibenzoyloxy-5-hydroxy-5α-cholestan-6-one (*IIIi*)

The triol *IIIh* (100 mg) was benzoylated with benzoyl chloride (0·1 ml) in pyridine (1 ml) at room temperature overnight. The mixture was decomposed with ice, the product taken up in ether and the ethereal solution was worked up as usual to afford the noncrystalline dibenzoate *IIIi* (98 mg), $[\alpha]_D^{20}$ −9° (*c* 1·8). IR spectrum: 1271, 1282, 1705 sh, 1725, 3470 cm^{-1}. CD spectrum: Δε −2·73, 305 nm; Δε +14·12, 236 nm. For $C_{41}H_{54}O_6$ (642·9) calculated: 76·60% C, 8·47% H; found: 76·67% C, 8·38% H.

2α,5-Epoxy-5α-cholestan-3-one (*IVa*)

The alcohol *IIf* (400 mg) was dissolved in dichloromethane (10 ml) and oxidized with Corey's oxidant[8] (800 mg) at room temperature overnight. The mixture was then passed through a column of aluminum oxide, the solvent was evaporated and the residue was crystallized from acetone–methanol–water to afford the ketone *IVa* (170 mg), m.p. 162−163°C, $[\alpha]_D^{20}$ +55° (*c* 2·1) in accordance with the literature[4]. IR spectrum: 1407, 1768 cm^{-1}. CD spectrum: Δε −0·25, 310 nm.

2α,5-Epoxy-5α-cholestane-3,6-dione (*IVb*)

a) *From* 2α,5-*epoxy*-3α-*hydroxy*-5α-*cholestan*-6-*one* (IIg): The alcohol *IIg* (200 mg) was dissolved in dichloromethane (5 ml) and oxidized, while stirring, with Corey's oxidant[8] (400 mg) at room temperature overnight. The mixture was filtered through a column of aluminum oxide, the solvent evaporated and the residue crystallized from methanol to yield the diketone *IVb*

(86 mg), m.p. 101–103°C, $[\alpha]_D^{20}$ +18° (*c* 1·9). IR spectrum: 1722, 1775 cm^{-1}. For $C_{27}H_{42}O_3$ (414·6) calculated: 78·21% C, 10·21% H; found: 78·42% C, 9·80% H.

b) *From* 2α,5-*epoxy*-5α-*cholestane*-3α,6β-*diol* (IIh): The diol *IIh* (20 mg) was dissolved in dichloromethane (3 ml) and oxidized with Corey's oxidant[8] (40 mg) as given above to afford the diketone *IVb* (6 mg), m.p. 100–102°C.

5α-Cholestan-2β,3β,5,6β-tetraol (*VII*)

a) *From* 2β,3β-*diacetoxy*-5-*hydroxy*-5α-*cholestan*-6-*one* (IIIb): The acetate *IIIb* (100 mg) in ether (10 ml) was refluxed with lithium aluminum hydride (100 mg) for 30 min. The mixture was decomposed with saturated aqueous sodium sulfate solution, the product extracted with ether and the ethereal solution worked up as usual. The residue was crystallized from a mixture of acetone, methanol and water to give the tetraol *VII* (21 mg), m.p. 261–263°C, $[\alpha]_D^{20}$ +15° (*c* 2·0). (literature reports[7] 255–256°C).

b) *From* 5α-*cholestane*-2β,3β,5,6β-*tetraol* 2,3-*diacetate* 6-*benzoate* (IIIc): The triester *IIIc* (100 mg) in ether (10 ml) was refluxed with lithium aluminum hydride (100 mg) for 30 min. The mixture was worked up as given under *a*) to yield the tetraol *VII* (29 mg), m.p. 264–266°C.

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Translated by the author (V. Č.).

Note added in proof: After submitting the manuscript to the press, the following two papers were published dealing with Woodward addition to *Ib* under formation of *IIIb*: 1) Alston K. T., Bebbington P. M., Green S. E., Morgan E. D., Poole C. F.: Steroids *27*, 609 (1976). 2) Glotter E., Schwartz A.: J. Chem. Soc., Perkin Trans. 1, *1976*, 1660. Transannular participation of the 5α-hydroxyl is not reported.