Calciferol and its Relatives. Part 26.[1] A Conversion of Cholesterol into 8-Hydroxymethyl-des-*AB*-cholest-8-ene

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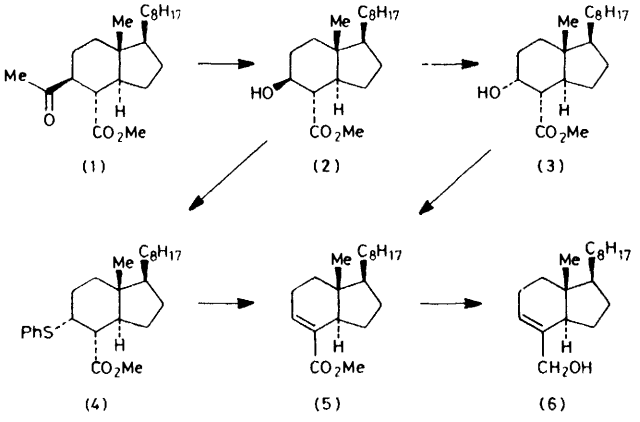
The methoxy-ketone (7), derived from Westphalen's diol, was degraded to 8α-benzoyloxymethyl-des-*AB*-cholestan-9-one (10), from which the title compound (6) was obtained in a yield of 47% based on the ketone (7), or 22.5% overall from cholesterol. The allylic alcohol (6) thus becomes relatively easily accessible.

THE present work, like that of the preceding paper, was motivated by the wish to obtain the allylic alcohol (6) and its relatives by a convenient route from readily available steroids.

In a previous degradative sequence [2] we converted cholesterol into methyl duoannelate (1), which was subjected to Baeyer–Villiger oxidation and methanolysis of the product to give the 9β-hydroxy-ester (2) in about 20% yield from cholesterol. This ester was then converted successively into its 9α-epimer (3) and the unsaturated ester (5). These last steps were inefficient, and we have since improved the route to the ester (5) by first treating the 9β-hydroxy-compound (2) with *N*-(phenylthio)succinimide [3] and tri-n-butylphosphine to give the 9α-phenylthio-compound (4). Treatment of the corresponding sulphone with methanolic sodium methoxide gave the ester (5) in good yield, and by reduction



with di-isobutylaluminium hydride we obtained the allylic alcohol (6) as the crystalline *p*-nitrobenzoate in 64% yield from the ester (2), or about 12% overall from cholesterol. Although this represented a substantial improvement, some of the steps leading to the ester (2) remained inconvenient, and we therefore investigated a different route described below.

RESULTS AND DISCUSSION

For this route the ketone (7) [4] was chosen as the starting material, since it possesses structural features which facilitate cleavage of the C(9)–C(10) and C(6)–C(7) bonds. It can be obtained in about 48% yield from cholesterol by converting cholesteryl methyl ether into 6β-acetoxy-3β-methoxycholestan-5α-ol, subjecting this to the Westphalen rearrangement, hydrolysing the product, and oxidising the free 6β-hydroxy-group to give the 6-oxo-compound (7).

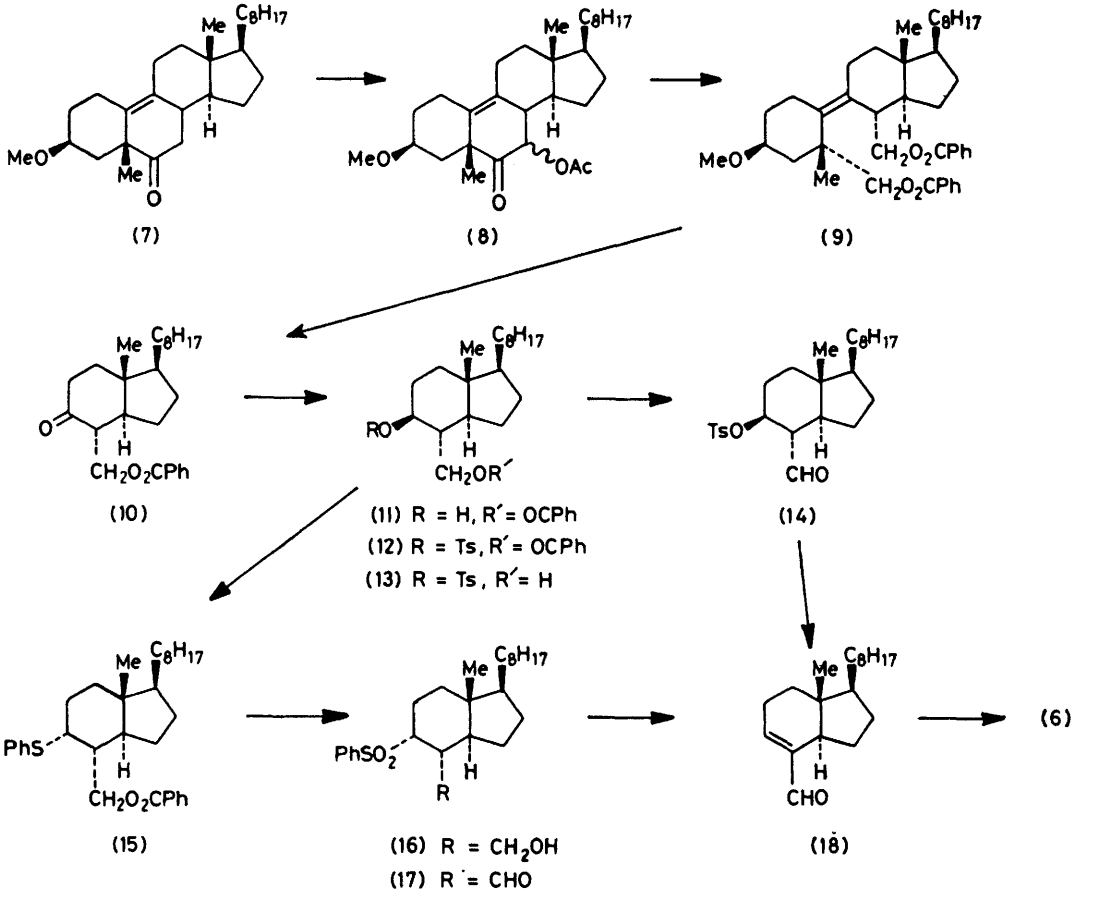
Using a procedure analogous to that of Rubottom,[5] the trimethylsilyl enol ether of the ketone (7) was treated with lead tetra-acetate in the presence of triethylammonium fluoride to give, in good yield, a mixture of the epimeric 7-acetoxyketones (8). Reduction with lithium aluminium hydride gave a mixture of 6,7-diols which were cleaved with lead tetra-acetate, and the product was reduced with lithium aluminium hydride, and then benzoylated to give the 6,7-seco-dibenzoate (9). This was subjected to ozonolysis in dichloromethane and methanol, with work-up using dimethyl sulphide, to give a mixture of the keto-benzoate (10) and 2-benzoyloxymethyl-4-methoxy-2-methylcyclohexanone. The sequence from the ketone (7) to this mixture was conducted without purification of products, but at this stage chromatography on silica gel was necessary in order to separate the ring-A cyclohexanone from the less polar keto-benzoate (10), which was so obtained in a yield of 71% from the ketone (7).

Reduction of the ketone (10) with lithium tri-t-butoxyaluminium hydride gave as the principal (95%) product the 9β-hydroxy-compound (11). In some experiments the minor product, the 9α-epimer of (11), was separated chromatographically, oxidised to the ketone (10), and so re-cycled. In our first experiments with the 9β-epimer (11) it was converted by Walker's method [3] into the 9α-phenylthio-benzoate (15), and then, by hydrolysis followed by oxidation of the phenylthio-group, into the sulphone (16). Oxidation of the primary hydroxy-group gave the aldehyde (17), which on filtration through basic alumina underwent elimination of the phenylsulphonyl group and yielded the αβ-unsaturated aldehyde (18). The sequence was completed by reduction of the aldehyde with di-isobutylaluminium hydride, and isolation of the allylic alcohol (6) as the *p*-nitrobenzoate in 58.5% yield from the keto-benzoate (10).

In later experiments the 9β-hydroxy-compound (11) was converted into the crystalline toluene-*p*-sulphonate (12), which on mild hydrolysis provided the alcohol (13). Oxidation to the corresponding aldehyde (14) by Swern's method,[6] and warming in dimethyl sulphoxide with potassium fluoride and sodium acetate, gave the αβ-

unsaturated aldehyde (18). From this, the *p*-nitrobenzoate of the allylic alcohol (6) was obtained in a yield of 66% based on the keto-benzoate (10), or 22.5% overall from cholesterol.

It is apparent that a similar sequence to that here described should allow the conversion of steroids such as 3β-hydroxy-5-cholenic acid, or stigmasterol or its side-chain degradation products, into side-chain hydroxylated derivatives of the allylic alcohol (6), including the 25-hydroxy-derivative. The alcohol (6) itself now becomes relatively easily accessible, so opening the way for its use in the work to be reported in Part 27.



EXPERIMENTAL

Unless otherwise specified, light petroleum refers to the fraction of b.p. 60—80 °C, and i.r. data refer to solutions in carbon tetrachloride. Optical rotations were measured for solutions in chloroform, and n.m.r. data for solutions in deuteriochloroform. T.l.c. and p.l.c. were carried out with Kieselgel GF_{254}.

Conversion of the 9β-Hydroxy-ester (2) *into the Allylic Alcohol* (6).—*N*-(Phenylthio)succinimide (2.69 g) and benzene (15 cm³) were stirred together and tri-n-butylphosphine (2.62 g) was added dropwise, followed, after 5 min, by the 9β-hydroxy-ester (2) (2.82 g). The mixture was kept at 23 °C for 48 h and then diluted with ether (50 cm³) and washed with 2N aqueous sodium hydroxide (3 × 25 cm³) and then water. Evaporation of the dried ethereal solution under reduced pressure and chromatography of the residue on silica gel (dichloromethane) gave the 9α-phenylthio-compound (4) as an oil (3.20 g, 88%); $\nu_{max.}$ 1 745 cm^{-1}; τ 2.5—2.8 (5 H, m, ArH), 6.15 (1 H, br, PhSC*H*), 6.50 (3 H, s, OMe), and 7.17 (1 H, dd, *J* 12 and 5 Hz, MeO_2CCH).

The phenylthio-compound (4) (3.50 g) was stirred with methyl chloride (40 cm³) at 23 °C during the portionwise addition of 85% *m*-chloroperbenzoic acid (3.60 g). Work-up in the usual way gave the corresponding 8α-phenylsulphonyl compound (3.85 g); $\nu_{max.}$ 1 155s, 1 310s, and 1 730s cm^{-1}; τ 2.0—2.5 (5 H, m, Ar-H), 6.2 (1 H, m, $PhSO_2CH$), 6.34 (3 H, s, OMe), and 2.87 (1 H, dd, *J* 13 and 6 Hz, MeO_2CCH).

A solution of the 8α-phenylsulphonyl compound (3.35 g) in 0.214N methanolic sodium methoxide (70 cm³) was kept at 23 °C for 12 h; glacial acetic acid (0.5 cm³) was then added, the solvent was removed under reduced pressure, and the residue was partitioned between light petroleum and water. The petroleum phase was dried and evaporated, giving the unsaturated ester (5) (2.33 g); after bulb-to-bulb distillation at 145 °C (bath temperature) and 0.05 mmHg it had $\nu_{max.}$ (film) 1 240s, 1 630w, and 1 715s cm^{-1}; τ 3.18 (1 H, m, =CH) and 6.30 (3 H, s, OMe).

The ester (5) (2.31 g), dissolved in light petroleum (20 cm³), was added dropwise to a stirred and cooled (0 °C) solution of di-isobutylaluminium hydride in hexane (20%; 20 cm³). The mixture was kept at 23 °C for 10 h, and then stirred and treated dropwise with methanol (8 cm³); after

a further 2 h, ethyl acetate (20 cm³) was added, and stirring was continued for 0.5 h. The mixture was filtered (Celite), solvents were removed under reduced pressure, and the residue was treated with *p*-nitrobenzoyl chloride (1.5 g) in pyridine (10 cm³) in the usual way. The *p*-nitrobenzoate of 8-hydroxymethyl-des-*AB*-cholest-8-ene (6) was filtered through a short column of silica gel (dichloromethane) and recrystallised from ethanol giving plates (2.37 g, 80%), m.p. 100.5—103.5 °C; $\nu_{max.}$ (CCl_4) 1 370s and 1 725s cm^{-1}; τ 4.3 (1 H, br, =CH) and 5.25 (2 H, s, CH_2OH).

3β-*Methoxy*-5β-*methyl*-19-*norcholest*-9-*en*-6-*one* (7).—Commercial cholesterol was treated with sodium hydride in dimethyl sulphoxide, and then with methyl iodide, which gave cholesteryl methyl ether (93%). It was hydroxylated with performic acid, followed by hydrolysis with aqueous sodium hydroxide; acetylation with pyridine and acetic anhydride then gave 6β-acetoxy-3β-methoxycholestan-5α-ol (88%). Rearrangement with sulphuric acid in acetic anhydride [7] gave 6β-acetoxy-3β-methoxy-5β-methyl-19-norcholest-9-ene (63%), which was hydrolysed with potassium hydroxide in methanol and benzene to give 6β-hydroxy-3β-methoxy-5β-methyl-19-norcholest-9-ene (96%). Oxidation by Swern's [6] method gave the ketone (7) (97%), m.p. 65—67 °C (lit.,[4] 65—66 °C); $\nu_{max.}$ 1 715s cm^{-1}; τ 6.68 (3 H, s, OMe), 8.63 (3 H, s, Me), and 9.24 (3 H, s, Me).

3β-*Methoxy*-5β-*methyl*-19-*norcholesta*-6,9-*diene*.—In one experiment the ketone (7) (828 mg) in dry tetrahydrofuran (5 cm³) was added to a stirred solution of lithium di-isopropylamide [from 1.6M-n-butyl-lithium in hexane (1.8 cm³) and di-isopropylamine (240 mg)] in tetrahydrofuran at −70 °C under nitrogen. After 15 min diethylphosphorochloridate (480 mg) in tetrahydrofuran (5 cm³) was added, and the mixture was allowed to warm to 20 °C (0.5 h) and stirred for a further 1 h, after which water (1 cm³) was added. Solvents were removed under reduced pressure, ether was added, and the solution was washed with aqueous sodium carbonate, dried, and evaporated. The oily enol phosphate (1.028 g) was homogeneous to t.l.c. (chloroform); $\nu_{max.}$ 960m, 1 040s, and 1 270m cm^{-1}; τ 4.66 (1 H, m, =CH), 6.67 (3 H, s, OMe), and 8.57 (3 H, s, Me) (Found: M^+, 550.380 7. Calc. for $C_{32}H_{55}O_5P$: *M*, 550.378 7). The enol phosphate (1.028 g) in tetrahydrofuran (20 cm³) and t-butyl alcohol (700 mg) was added (0.5 h) to a stirred solution of lithium (140 mg) in ethylamine (20 cm³) at −10 °C under nitrogen. The mixture was allowed to warm to 0 °C, and after 0.5 h saturated aqueous ammonium chloride was added, and solvents were removed under reduced pressure. The product, isolated with ether and dissolved in benzene–light petroleum (1 : 1) was passed through a short column of silica gel. Evaporation of the solution gave 3β-*methoxy*-5β-*methyl*-19-*norcholesta*-6,9-*diene* (670 mg), m.p. 51 °C; $[\alpha]_D^{21}$ −33.5°; $\nu_{max.}$ (KCl) 718m, 743m, 988m, 1 085s, 1 115s, 1 187m, 1 215m, 1 364s, 1 385m, and 1 467s cm^{-1}; τ 4.64 (2 H, s, =CH), 6.50 (1 H, m, C*H*OH), 6.68 (3 H, s, OMe), 8.76 (3 H, s, Me), and 9.19 (s, Me) (Found: C, 84.2; H, 11.8. $C_{28}H_{46}O$ requires C, 84.35; H, 11.65%). This diene was also obtained (with J. Tideswell) by reaction of 3β-methoxy-5β-methyl-19-norcholest-9-en-6α-ol with phosphoryl chloride in pyridine.

8α-*Benzoyloxymethyl*-*des*-AB-*cholestan*-9-*one* (10).—A solution of lithium di-isopropylamide, prepared from di-isopropylamine (3.34 g) and 1.6M n-butyl-lithium in hexane (20.6 cm³), in tetrahydrofuran (25 cm³) was stirred and cooled to −70 °C during the dropwise addition of a solution of the ketone (7) (6.82 g) in tetrahydrofuran (25 cm³). After a further 15 min at −70 °C trimethylsilyl chloride (10 cm³) was added in one portion, and the mixture was allowed to attain room temperature. It was distributed at 0 °C between light petroleum (300 cm³) and aqueous sodium hydrogencarbonate; the petroleum phase was then washed with ice–water, and was dried and evaporated under reduced pressure. The crystalline product, which t.l.c. showed to be homogeneous, was used without purification for the next step. In one experiment this product was crystallised from light petroleum at −10 °C giving 3β-*methoxy*-5β-*methyl*-6-*trimethylsilyloxy*-19-*norcholesta*-6,9-*diene* as needles, m.p. 93.5—95 °C; $[\alpha]_D^{32}$ +9.5°, $\nu_{max.}$ 1 090m, 1 120m, 1 210s, 1 250m, and 1 470m cm^{-1}; τ 5.47 (1 H, d, *J* 3 Hz, =CH), 6.45 (1 H, m, C*H*OH), 6.65 (3 H, s, OMe), 8.63 (3 H, s, Me), 9.18 (3 H, s, Me), and 9.80 (9 H, s, $SiMe_3$) (Found: C, 76.75; H, 11.35. $C_{31}H_{54}O_2Si$ requires C, 76.5; H, 11.2%).

To a mixture of the above crude silyl ether and lead tetra-acetate (8.27 g) in methylene chloride (20 cm³) at 5 °C freshly distilled triethylammonium fluoride (5 cm³) was added with stirring; the temperature rose to 12 °C and a precipitate formed. After 3 h, excess of lead tetra-acetate was destroyed with ethylene glycol, the mixture was filtered through Celite, and the filtrate was diluted with ether (200 cm³) and was washed with 1N-hydrochloric acid (2 × 100 cm³) and aqueous sodium hydrogencarbonate, and dried and evaporated under reduced pressure to an oily mixture (7.55 g) of the epimeric acetoxy-ketones (8); $\nu_{max.}$ 1 240s, 1 470m, 1 730s, and 1 750s cm^{-1}; τ 4.21 [d, *J* 8 Hz, C(7)-H] and 4.74 [d, *J* 11 Hz, C(7)-H].

The oily acetoxy-ketones (8) (7.55 g) in ether (30 cm³) were added dropwise to lithium aluminium hydride (0.76 g) in ether (30 cm³). The mixture was heated under reflux for 1 h; it was then cooled and powdered sodium sulphate decahydrate (12 g) was added. The mixture was filtered and evaporated to give an oily mixture (6.80 g) of 6,7-diols. Its solution in methylene chloride (50 cm³) at 0 °C was stirred, and lead tetra-acetate (7.1 g) was added in portions during 10 min. After a further 10 min ethylene glycol (1 cm³) was added. The solution was decanted into ether (150 cm³) and was washed (1*N* HCl; then $NaHCO_3$ aqueous), dried, and evaporated. The residue, dissolved in ether (30 cm³), was added (10 min) to lithium aluminium hydride (600 mg) in ether (15 cm³), and the mixture was heated under reflux for 30 min. After normal work-up the product was kept in pyridine (50 cm³) with benzoyl chloride (4.2 g) for 3 h, and worked up as usual to give the oily seco-dibenzoate (9) (8.23 g) which was homogeneous to t.l.c.; $\nu_{max.}$ 710s, 1 105s, 1 270s, 1 455m, and 1 725s cm^{-1}; τ 1.98 (4 H, m, Ar-H), 2.58 (6 H, m, Ar-H), 5.3—5.9 (4 H, m, CH_2O), 6.50 (1 H, m, CHO), 6.65 (3 H, s, OMe), and 8.33 (3 H, s, Me) (Found: M^+, 640.413 8. Calc. for $C_{42}H_{56}O_5$: *M*, 640.412 7).

The dibenzoate (9) (5.49 g) in methylene chloride (25 cm³) and methanol (25 cm³) was treated with ozonised oxygen at −78 °C until the solution was pale blue. Dimethyl sulphide (3 cm³) was then added, the mixture was allowed to attain room temperature, and after 3 h solvents were evaporated, and the residue was dissolved in ether. The solution was washed thoroughly with water, and was then dried and evaporated. Chromatography of the residue on silica gel (5 × 15 cm) in light petroleum, and elution with 10% ethyl acetate–light petroleum gave the *keto-benzoate* (10) as an oil [3.12 g, 71% overall from (7)] which was homogeneous to t.l.c.; $\nu_{max.}$ 1 110m, 1 275s, 1 460m, and

1 720s cm^{-1}; τ 5.38 (1 H, dd, *J* 5 and 12 Hz, C*H*OBz), 5.54 (1 H, dd, *J* 3 and 12 Hz, C*H*OBz), and 8.98 (3 H, s, Me) (Found: M^+, 398.282 8. $C_{26}H_{38}O_3$ requires *M*, 398.282 1).

The more polar component from the chromatogram, 2-benzoyloxymethyl-4-methoxy-2-methylcyclohexanone, formed an oil; $\nu_{max.}$ 1 100m, 1 270s, 1 450w, and 1 725s cm^{-1}; τ 2.00 (2 H, m, Ar-H), 2.53 (3 H, m, Ar-H), 5.62 (2 H, s, CH_2OBz), 6.26 (1 H, m, C*H*OMe), 6.60 (3 H, s, OMe), and 8.69 (3 H, s, Me) (Found: M^+, 276.136 5. Calc. for $C_{16}H_{20}O_4$: *M*, 276.136 2).

The Hydroxy-benzoate (11).—The keto-benzoate (10) (1.025 g) dissolved in ether (5 cm^3) was added dropwise at room temperature to a stirred mixture prepared by adding t-butyl alcohol (666 mg) to lithium aluminium hydride (114 mg) in ether (5 cm^3). After 3 h the mixture was added to 1N-hydrochloric acid (20 cm^3) at 0 °C; the ether layer was washed with aqueous sodium hydrogencarbonate and water, then dried and evaporated. Chromatography on silica gel (benzene) gave the less polar product, 8α-benzoyloxymethyl-9α-hydroxy-des-*AB*-cholestane as an oil (61 mg); $\nu_{max.}$ 1 115m, 1 280s, 1 460m, 1 710s, and 1 725s cm^{-1}; τ 1.95 (2 H, m, Ar-H), 2.53 (3 H, m, Ar-H), 5.40 (d, *J* 12 Hz, with fine splitting, C*H*OBz), 5.81 (1 H, dd, *J* 5 and 12 Hz, C*H*OBz), 6.03br (1 H, s, $W_{\frac{1}{2}}$ 6 Hz, C*H*OH), and 9.27 (3 H, s, Me) (Found: M^+, 400.299 1. Calc. for $C_{26}H_{40}O_3$: *M*, 400.297 7). Oxidation of this material in the usual way with pyridinium chlorochromate gave the keto-benzoate (10) (90%). The more polar product from the chromatogram, 8α-benzoyloxymethyl-9β-hydroxy-des-*AB*-cholestane (11) formed an oil (0.989 g, 96%); $\nu_{max.}$ 1 110m, 1 275s, 1 460m, 1 710s, and 1 725s cm^{-1}, τ 1.97 (2 H, m, Ar-H), 2.55 (3 H, m, Ar-H), 5.29 (1 H, dd, *J* 4 and 12 Hz, C*H*OBz), 5.75 (1 H, dd, *J* 3 and 12 Hz, C*H*OBz), 6.60 (1 H, m, C*H*OH), and 9.23 (3 H, s, Me) (Found: M^+, 400.299 1).

The *toluene*-p-*sulphonate* (12) of the 9β-ol (11) was obtained by treatment of the mixed alcohols with toluene-*p*-sulphonyl chloride in pyridine [yield from the ketone (10), 91%]. Crystallisation from light petroleum gave material, m.p. 125—127 °C; $[\alpha]_D^{25}$ +61°; $\nu_{max.}$ 664m, 708m, 943m, 1 177s, 1 188m, 1 272s, 1 374m, 1 467w, and 1 725s cm^{-1}; τ 5.47 (1 H, m, C*H*OTs), 5.83 (1 H, dd, *J* 3 and 12 Hz, C*H*OBz), 6.01 (1 H, dd, *J* 3 and 12 Hz, C*H*OBz), 7.83 (3 H, s, Ar*Me*), and 9.21 (3 H, s, Me) (Found: C, 71.55; H, 8.5; S, 5.75. $C_{33}H_{46}O_5S$ requires C, 71.4; H, 8.4; S, 5.8%).

9α-*Phenylsulphonyl*-8α-*hydroxymethyl-des*-AB-*cholestane* (16).—The hydroxy-benzoate (11) (720 mg) in benzene (4 cm^3) was added to a stirred solution of *N*-(phenylthio)-succinimide (727 mg) and tri-n-butylphosphine (745 mg) in benzene (4 cm^3). After 48 h ether (25 cm^3) was added, and the mixture was washed with 2N aqueous sodium hydroxide and then water, and then dried and evaporated. Chromatography on silica gel (50% benzene–light petroleum) gave the phenylthio-compound (15) as an oil (817 mg, 93%). It was heated under reflux with methanol (10 cm^3), benzene (10 cm^3), and potassium hydroxide (0.5 g) for 20 min, after which the product was isolated with ether. The phenylthio-alcohol formed an oil (630 mg), homogeneous to t.l.c. A portion (572 mg) in methylene chloride (15 cm^3) at 0 °C was stirred with *m*-chloroperbenzoic acid (634 mg) for 0.5 h. The solvent was removed under reduced pressure, and the residue, dissolved in ether, was washed successively with aqueous sodium hydrogensulphite, aqueous sodium carbonate, and water, and the solution was dried and evaporated. The *hydroxy-sulphone* (16) formed an oil (600 mg, 97%), homogeneous to t.l.c.; $\nu_{max.}$ 635m, 690m, 1 135s, 1 310s, 1 450m, and 3 550s cm^{-1}; τ 2.10 (2 H, m, Ar-H), 2.40 (3 H, m, Ar-H), and 9.32 (3 H, s, Me) (Found: M^+, 420.268 5. $C_{25}H_{40}O_3S$ requires *M*, 420.269 8).

Conversion of the Sulphone (16) *into the Allylic Alcohol* (6).—Oxidation of the sulphone (16) (600 mg) with pyridinium chlorochromate (2 g) at room temperature for 10 h, with normal work-up, gave the aldehyde (17) as an oil (540 mg); $\nu_{max.}$ 1 720s cm^{-1}; τ 0.04 (1 H, br s, $W_{\frac{1}{2}}$ 5 Hz, CHO); it was homogeneous to t.l.c. It was dissolved in ether and filtered through a column of basic alumina (20 × 2 cm; Grade 1). Removal of ether from the filtrate under reduced pressure gave 8-formyl-des-*AB*-cholest-8-ene (18) as an oil (330 mg) which was essentially homogenous to t.l.c.; after a portion had been subjected to p.l.c. it had $\nu_{max.}$ 1 380w, 1 470w, 1 625w, 1 690s, and 2 705w cm^{-1}; $\lambda_{max.}$ (EtOH) 236 nm (ε 11 800); τ 0.60 (1 H, s, CHO), 3.35 (1 H, m, =CH), and 9.38 (3 H, s, Me). Reduction of the aldehyde (18) (330 mg) with di-isobutylaluminium hydride as described below, and esterification of the product with *p*-nitrobenzoyl chloride in pyridine, gave the *p*-nitrobenzoate of 8-hydroxymethyl-des-*AB*-cholest-8-ene (6) as plates [310 mg, 70% from (16)] (from ethanol), m.p. 102.5—104 °C.

9β-*Toluene*-p-*sulphonyloxy*-8α-*formyl-des*-AB-*cholestane* (14).—The benzoate (12) (420 mg) was dissolved in tetrahydrofuran (1.5 cm^3) and methanol (1.5 cm^3), and was kept at room temperature for 16 h with a solution of potassium hydroxide (180 mg) in the minimum volume of water. The solvents were removed under reduced pressure and the residue was worked up with water and ether in the usual way, giving the hydroxy-toluene-*p*-sulphonate (13) as a waxy solid (330 mg, 97%), homogeneous to t.l.c. It was added with stirring to a mixture at −78 °C prepared by the dropwise addition of dimethyl sulphoxide (156 mg) to oxalyl chloride (127 mg) in methylene chloride (3 cm^3) at −78 °C. After 10 min, triethylamine (505 mg) was added, and stirring was continued for a further 30 min; the mixture was then allowed to warm to room temperature and was poured into ether (15 cm^3). The solution was washed with water, 1N hydrochloric acid, and aqueous sodium hydrogencarbonate, and was dried and evaporated under reduced pressure. Crystallisation of the residue from light petroleum (b.p. 30—40°) gave the *tosyloxy-aldehyde* (14) (307 mg, 93%), m.p. 65—67 °C; $[\alpha]_D^{18}$ +28.5°; $\nu_{max.}$ 1 175s, 1 190s, 1 375s, and 1 730s cm^{-1}, τ 0.68 (1 H, d, *J* 4 Hz, CHO), 2.22 (2 H, d, *J* 9 Hz, Ar-H), 2.66 (2 H, d, *J* 9 Hz, Ar-H), 5.20 (1 H, m, C*H*OTs), 7.54 (3 H, s, Ar-Me), and 9.24 (3 H, s, Me) (Found: C, 69.5; H, 9.15; S, 7.3. $C_{26}H_{40}O_4S$ requires C, 69.6; H, 9.0; S, 7.1%).

Conversion of the Toluene-p-*sulphonate* (14) *into the Alcohol* (6).—The toluene-*p*-sulphonate (14) (307 mg), anhydrous potassium fluoride (122 mg), and anhydrous sodium acetate (82 mg) were stirred together in dry dimethyl sulphoxide (3 cm^3) under nitrogen at 60 °C for 36 h. The cooled mixture was poured into water (10 cm^3) and extracted with light petroleum (2 × 10 cm^3). The petroleum extract was washed with water, dried, and evaporated to low volume (5 cm^3). To this solution at 0 °C 1M di-isobutylaluminium hydride in hexane (1 cm^3) was added; after 2 h at 0 °C the mixture was added to stirred 1N hydrochloric acid (10 cm^3) at 0 °C. The organic phase was washed with aqueous sodium hydrogencarbonate, and was dried and evaporated. The residue was kept with *p*-nitrobenzoyl chloride (185 mg) in pyridine (2 cm^3) at 23 °C for 8 h. Normal work-up gave the *p*-nitrobenzoate of the alcohol (6)

[236 mg, 81% from the tosylate (14)] as plates (from ethanol), m.p. 100—103 °C (lit.,[2] m.p. 103 °C).

We thank the S.R.C. for a post-doctoral award (P. J. K.) and a studentship (D. A. R.).

[9/1046 *Received*, 4*th July*, 1979]

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