# Reactions of Relevance to the Chemistry of Aminoglycoside Antibiotics. Part 13.† A Novel Synthesis of Benzyl Ethers

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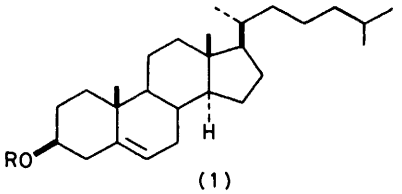
Benzyl ethers were prepared from alcohols by reaction with chloro(phenylmethylene)dimethylammonium chloride and sodium hydrogen telluride in sequence. The salt (1) [$Me_2NC(R^1)OR^2Cl^-$; $R^1$ = H, $R^2$ = cholest-5-en-3β-yl] and sodium borohydride gave the borane complex of 3β-dimethylaminomethoxycholest-5-ene. Salt (1; $R^1$ = Ph, $R^2$ = cholest-5-en-3β-yl or 5α-cholestan-3β-yl) and ammonia or hydrazine gave the steroidal benzimidates or benzhydrazonate.

3β-BENZYLOXYCHOLEST-5-ENE (1a) has been prepared by the reaction of sodium hydrogen telluride with cholest-5-en-3β-yloxy(phenylmethylene)dimethylammonium chloride (1b).[1] Most probably the reaction proceeds *via* intermediacy of the tellurobenzoate (1c) and electron transfer (Scheme). This reaction provides a mild non-basic procedure for the introduction of the benzyl group, important for hydroxy-protection in carbohydrates. Herein is reported a more detailed study of this and related reactions.



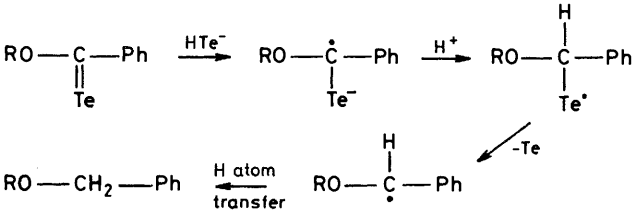
(1)

a; R = $PhCH_2$
b; R = $Cl^-$ $Me_2\overset{+}{N}=CPh$
c; R = PhC (=Te)
d; R = $Cl^-$ $Me_2\overset{+}{N}=CH$
e; R = HC(=Te)
f; R = $CH_2$·
g; R = PhCH·
h; R = H
i; R = $Me_2NCH_2$·$BH_3$
j; R = $Cl^-$ $Me_2\overset{+}{N}HCH_2$·$BH_3$
k; R = HCO
l; R = Me
m; R = HC(=Se)
n; R = $Me_2NCH(Ph)$
o; R = $Me_2NCH_2$
p; R = PhC(=NH)
q; R = PhC(=NTs)
r; R = $PhC(=NSO_2CF_3)$
s; R = $PhC(=NCOCF_3)$
t; R = PhCO
u; R = PhC(=Se)

5α-Cholestan-3β-ol (2a) was converted into cholestan-3β-yloxy(phenylmethylene)dimethylammonium chloride (2b) using standard Vilsmeier methodology.[1] This on reaction with sodium hydrogen telluride buffered with acetic acid gave the known 3β-benzyloxy-5α-cholestane (2c)[2] and tellurium. Similarly ergosterol (3a) was converted into 3β-benzyloxyergosta-5,7,22-triene (3b). The hindered 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (4a) gave the known[3] derived benzyl ether (4b).

† Part 12, D. H. R. Barton and W. B. Motherwell, *J.C.S. Perkin I*, 1980, 1124.

Reaction of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (5a) with the Vilsmeier salt (6a) (2.6 equiv.) for 12 h and subsequently with sodium hydrogen telluride gave a mixture of three major products. Chromato-

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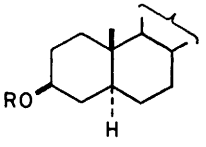
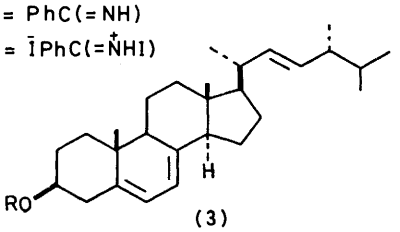
graphy gave the known[4] dibenzyl (5b) (27%), the 2-benzyl (5c) (25%) and the 3-benzyl derivatives (5d) (19%). Structural assignment followed from comparison with literature data with one exception; we observed



(2)

a; R = H
b; R = $Cl^-$ $Me_2\overset{+}{N}=C(Ph)$
c; R = $PhCH_2$
d; R = $(PHCH)_2$
e; R = $PhC\overset{\cdot}{H}$
f; R = PhC(=Te)
g; R = PhC(=NH)
h; R = $\bar{I}PhC(=\overset{+}{N}HI)$
i; R = $PhC(=N_2)$
j; R = $(PhC=N)_2$
k; R = $PhC(=NNH_2)$
l; R = Ac
m; R = $PhC(=NNAc_2)$
n; R = PhCO

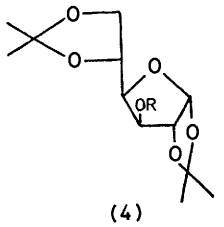


(3)

a; R = H
b R = $PhCH_2$

$[\alpha]_D^{23}$ +33° for isomer (5c) (lit.,[5] +4.0°); the m.p.s were in agreement. The blank reaction showed that formation of the di-imidate salt (5e) was sluggish and incomplete. The diol (5a), pyridine, and chloro-

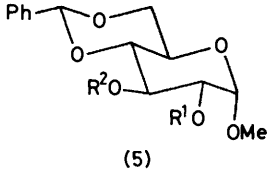
(phenylmethylene)dimethylammonium chloride (6a) on reaction in dichloromethane for 1 h gave, on hydrolytic work up, mostly the 3-benzoate (5f) [5] with little dibenzoate (5g) or 2-benzoate (5h); this has precedent.[5] The addition of imidazole but not *N,N,N′,N′*-tetramethylguanidine accelerated the reaction and after 6 h



(4)

a; R = H

b; R = $PhCH_2$



(5)

a; $R^1 = R^2 = H$

b; $R^1 = R^2 = PhCH_2$

c; $R^1 = PhCH_2$, $R^2 = H$

d; $R^1 = H$, $R^2 = PhCH_2$

e; $R^1 = R^2 = Cl^-Me_2\overset{+}{N}=C(Ph)$

f; $R^1 = H$, $R^2 = PhCO$

g; $R^1 = R^2 = PhCO$

h; $R^1 = PhCO$, $R^2 = H$

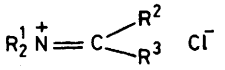
i; $R^1 = R^2 = PhC(=S)$

j; $R^1 = R^2 = PhC(=Se)$

k; $R^1 = PhCO$, $R^2 = PhC(=Se)$

l; $R^1 = H$, $R^2 = PhC(=Se)$

aqueous work up gave the known [6] dibenzoate (5g) (73%). Clearly the formation of the di-imidate salt (5e) must be decelerated by steric congestion. We suggest that the imidazole catalysis involved the imidate salt (6c). When the diol (5a) was treated with the Vilsmeier salt (6a), imidazole, and pyridine followed by sodium hydrogen telluride, again the dibenzyl (5b) (28%), 2-benzyl (5c) (11%), and 3-benzyl derivatives (5d) (11%) were formed. Exclusive formation of the dibenzyl derivative (5b) was never achieved. The Vilsmeier salt (6d) derived from *N*-benzoylpyrrolidine was examined. Reaction with the diol (5a), imidazole, and pyridine followed by hydrogen sulphide gave the bis-thiobenzoate (5i) (61%) identical with authentic material.[1] Unexpectedly the reaction of the diol (5a) with the Vilsmeier salt (6a), pyridine, and imidazole followed by sodium hydrogen selenide [1] gave a minor product, possibly the bis-selenobenzoate (5j) (7%), and a monobenzoyl-monoselenobenzoyl derivative [($C_{28}H_{26}O_7Se$ (microanalysis and the mass spectrum)]. This was most reasonably [n.m.r., δ 5.5 (1 H, dd, $J_{1,2}$ 4 Hz, $J_{2,3}$ 10.5 Hz, 2-H)] the 2-benzoyl-3-selenobenzoyl derivative (5k). This was confirmed by the benzoylation (PhCOCl–pyridine) of authentic [1] methyl 4,6-*O*-benzylidene-3-*O*-selenobenzoyl-α-D-glucopyranoside (5l). Clearly the low yield of the dibenzyl derivative (5b) resulted from inefficient reduction with sodium hydrogen telluride; alternative reducing systems were examined. Contamination of the sodium hydrogen telluride with boron compounds may have complicated the di-imidate (5e) reduction. Elsewhere [7] we reported the efficiency of potassium and 18-crown-6 as a reducing system. Tellurium was reduced by potassium and 18-crown-6 in 1,2-dimethoxyethane (DME) under nitrogen giving a clear solution, presumably containing potassium hydrogen telluride, after buffering with acetic acid. The addition of the imidate salt (2b) (0.33 equiv.) gave tellurium and a solid, m.p. 265—270 °C, $[\alpha]_D^{21}$ +15°. The analysis ($C_{68}H_{106}O_2$) and the mass spectrum [$M^+$ absent, 566 ($M^+$ − 5α-cholestanol)] were consistent with formulation as the dihydrobenzoin diether (2d) formed *via* radical (2e) capture by the telluro-ester (2f). Reduction of the imidate salt (2b) with potassium hydrogen telluride (20 equiv.) and 18-crown-6 in DME gave the diether (2d) (12%) and 3β-benzyloxy-5α-cholestane (2c) (74%). Dichloromethane reacted rapidly with potassium hydrogen telluride and 18-crown-6 and was an unsuitable co-solvent. Reduction of the di-imidate



(6)

a; $R^1 = Me$, $R^2 = Ph$, $R^3 = Cl$

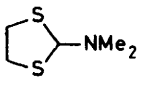
b; $R^1 = Me$, $R^2 = H$, $R^3 = Cl$

c; $R^1 = Me$, $R^2 = Ph$, $R^3 =$ 

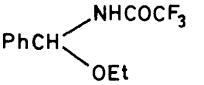
d; $R_2^1 = [CH_2]_4$, $R^2 = Ph$, $R^3 = Cl$

e; $R^1 = Me$, $R^2 = Ph$, $R^3 = H$

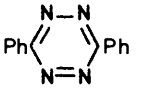
f; $R^1 = Me$, $R^2 = R^3 = H$



(7)



(8)



(9)

salt (5e) with potassium hydrogen telluride and 18-crown-6 gave a complex mixture.

Previously [1] we have reported that the sodium hydrogen telluride reduction of cholest-5-en-3β-yloxy(methylene)dimethylammonium chloride (1d) gave an uncharacterised unstable telluriferous species. Telluroformates [*e.g.* (1e)] should be less susceptible to reduction by electron transfer from the hydrogen telluride anion on account of radical (1f) being less stable than (1g). We have re-investigated this reaction. The imidate salt (1d) with sodium hydrogen telluride with or without acetic acid in ethanol–dichloromethane or DME–ethanol, followed by quenching with (a) iodomethane at −10 °C, (b) iodomethane then sodium borohydride or cyano-

borohydride at −20 °C, (c) nickel boride, or (d) lithium aluminium hydride gave mostly cholesterol (1h) and only minor, unstable tellurium-containing species that decomposed to regenerate more cholesterol (1h). No stable products derived from the telluroformate (1e) could be isolated. In a blank experiment the imidate salt (1d) was reduced with sodium borohydride to give a stable crystalline solid ($C_{30}H_{56}BNO$), m.p. 155—158 °C, $[\alpha]_D^{20}$ −31.2°. This was assigned as the borane complex of 3β-dimethylaminomethoxycholest-5-ene (1i) [*inter alia* $\nu_{max.}$ (2 360 and 2 270 $cm^{-1}$); δ 5.3 (1 H, m, 6-H), 5.0—3.0 (6 H, m, 3α-H, $OCH_2$, $BH_3$), and 2.57 (6 H, s, $NMe_2$)]. The complex was surprisingly stable; treatment with anhydrous hydrogen chloride gave the microanalytically pure hydrochloride, possibly structure (1j). Complex (1i) was only slowly decomposed by aqueous acetic or trichloroacetic acid, or sodium hydrogen carbonate or sodium hydroxide in THF. Cholesterol (1h) was rapidly regenerated when the complex was heated under reflux with benzyl bromide in ethanol, allowed to react with methyl toluene-4-sulphonate in diglyme at 100 °C, oxidized with diphenyl seleninic anhydride,[8] mercury(II) salts, or quinones, or when heated under reflux in cyclohexene. Attempted reduction of the imidate salt (1d) with sodium cyanoborohydride in ethanol or lithium tri-t-butoxyaluminium hydride in diethyl ether gave only cholesterol (1h). The imidate salt (1d) and triethylammonium formate [9] in dichloromethane–THF or DMF gave only the formate (1k). Clearly the imidate salt (1d) was not a suitable precursor for 3β-methoxycholest-5-ene (1l) except *via* cholest-5-en-3β-yl selenoformate (1m).[2]

Cholest-5-en-3β-yloxy(phenylmethylene)dimethylammonium chloride (1b) on reaction with sodium borohydride in ethanol gave cholesterol (1h) and *N*,*N*-dimethylbenzylamine only. Borane complexes were not detected. Presumably the intermediate ether (1n) lost cholesterol (1h) more rapidly than its capture by borane; ether (1n) is more sterically congested than (1o) and benzylidenedimethylammonium chloride (6e) more stable than methylenedimethylammonium chloride (6f).

Conversion of an alcohol into a 2-alkoxy-1,3-dithiolan by Vilsmeier methodology would provide a convenient synthesis of methyl ethers after nickel boride desulphurisation. Thus ethane-1,2-dithiol was added to the imidate salt (1d). Aqueous work-up gave cholesterol (1h) and 2-dimethylamino-1,3-dithiolan (7) (54%). The blank reaction between chloromethylenedimethylammonium chloride (6b) and ethane-1,2-dithiol gave the same dithiolan derivative (7).

Benzimidate derivatives *N*-substituted by an electron-withdrawing group should provide *O*-alkyl thiobenzoates, selenobenzoates, or benzyl ethers on reaction with hydrogen sulphide–pyridine, sodium hydrogen selenide or telluride respectively. Vilsmeier methodology should provide easy access to these benzimidates. As expected, reaction of the imidate salt (1b) with an excess of ammonium chloride and triethylamine gave cholest-5-en-3β-yl benzimidate (1p) (92%). Microanalysis and spectral data [$\nu_{max.}$ 3 320, 1 630, and 1 580 $cm^{-1}$; *m/e* 489 ($M^+$)] were consistent with the structural assignment. 5α-Cholestan-3β-ol (2a) likewise gave 5α-cholestan-3β-yl benzimidate (2g) (83%). Cholest-5-en-3β-yl benzimidate (1p) reacted with toluene-4- and trifluoromethanesulphonyl chlorides to give respectively the fully characterised *N*-toluene-4- (1q) and *N*-trifluoromethane- (1r) sulphonyl derivatives. The benzimidate (1p) and trifluoroacetic anhydride gave an unstable crystalline solid, m.p. 110—117 °C, *m/e* 585 ($M^+$) which was most probably the *N*-trifluoroacetyl derivative (1s). Reaction, however, of the *N*-trifluoroacetyl derivative (1s) *in situ* or the *N*-trifluoromethanesulphonyl analogue (1r) with sodium hydrogen telluride or selenide usually gave intractable mixtures; components co-chromatographing with cholest-5-en-3β-yl benzoate (1t), selenobenzoate (1u), and 3β-benzyloxycholest-5-ene (1a) were detected. The trifluoroacetyl derivative (1s) and sodium hydrogen telluride gave a non-steroidal product isolated by sublimation. This was assigned as ethoxy(trifluoroacetamido)methylbenzene (8) by comparison with authentic material. Ethyl benzimidate on reaction with trifluoroacetic anhydride and subsequently sodium borohydride gave the same carbinolamine derivative (8). 5α-Cholestan-3β-yl benzimidate (2g) and iodine gave 3α-iodo-5α-cholestane, identical with authentic material (mixed m.p.), possibly formed *via* the salt (2h) and $S_N2$ attack by iodide anion.

Di-t-butyl selenone is available from di-t-butyldiazomethane and elemental selenium. Possibly selenobenzoates and even tellurobenzoates may be prepared from 1-alkoxy-1-phenyldiazomethane and selenium or tellurium. Thus the synthesis of 5α-cholestan-3β-yloxy-1-phenyldiazomethane (2i) was examined. Reaction of the imidate salt (2b), excess of hydrazinium chloride, and triethylamine gave *N*,*N*′-bis-[α-(5α-cholesten-3β-yloxy)benzylidene]hydrazine (2j) (13%) and 5β-cholestan-3β-yl benzohydrazonate (2k) (23%) separable by fractional crystallisation. Both were obtained microanalytically pure and exhibited molecular ions in the mass spectra. Chromatography of the aged mother-liquor gave a minor purple crystalline solid ($C_{14}H_{10}N_4$) clearly [*m/e* 234 ($M^+$), $\lambda_{max.}$ 294 nm (ε 21 000)] 3,6-diphenyl-1,2,4,5-tetrazine (9) formed *via* the dihydrotetrazine and aerial oxidation. A subsequent preparation gave the hydrazine (2j) (54%) and the benzohydrazonate (2k) (14%); in general the insoluble hydrazine (2j) was the major product. In this case acetylation of the mother-liquor followed by chromatography gave 5α-cholestan-3β-yl acetate (2l) (14%), 5α-cholestan-3β-yl *N*,*N*-diacetylbenzohydrazonate (2m) (1%) and a minor unidentified crystalline solid. The hydrazine (2m) [$\nu_{max.}$ 1 720, 1 700, 1 628, and 1 600 $cm^{-1}$, *m/e* 590 ($M^+$)] was obtained microanalytically pure. Attempted oxidation of the benzohydrazonate (2k) with mercury(II) oxide, manganese(IV) oxide, or dibromotriphenylphosphorane, failed to produce the required diazo-compound (2i) (i.r. or u.v.). 5α-Choles-

tan-3β-ol (2a) and its ester (2n) were the only detected products.

Clearly Vilsmeier methodology is amenable to facile syntheses of benzyl ethers, benzimidates, benzohydrazonates, and their derivatives under mild conditions.

## EXPERIMENTAL

M.p.s were determined on a Kofler hot stage. Optical rotations refer to chloroform solutions unless stated to the contrary; i.r. spectra were recorded as Nujol mulls (solids) or as liquid films, and n.m.r. spectra were recorded in deuteriochloroform with tetramethylsilane as an internal reference. Solvents and reagents were purified by standard procedures;[10] 1,2-dimethoxyethane (DME) was dried by reflux over potassium (12 h) and distillation directly into the reaction vessel. Reactions were carried out at room temperature under nitrogen unless otherwise stipulated. Light petroleum and petroleum refer to the redistilled reagents with respective b.p. 40—60 and 60—80 °C. Both selenium and tellurium were finely divided before use. Organic extracts were dried over anhydrous sodium sulphate and solvents removed by evaporation under reduced pressure. Repeated procedures are described in full in the first instance only.

*Preparation of Benzyl Ethers.*—*N,N*-Dimethylbenzamide (0.38 g, 2.5 mmol) in phosgene and dichloromethane (10%, w/v; 10 ml) were allowed to react overnight, solvent was evaporated (50 °C), and the residue dissolved in dichloromethane (10 ml). The alcohol (2.0 mmol) and triethylamine (0.3 ml, 2.0 mmol) in THF or dichloromethane (10 ml) were added over 5 min. Tellurium (0.65 g, 5.0 mmol) and sodium borohydride (0.45 g, 12 mmol) in ethanol (20 ml) were refluxed to complete dissolution (30—45 min). The telluride was cooled to −20 °C and deoxygenated acetic acid (0.60 ml, 10 mmol) added to buffer. When formation of the (alkoxyphenylmethylene)dimethylammonium chloride was complete (t.l.c.) the solution was added to the sodium hydrogen telluride at −20 °C. Tellurium was rapidly deposited. After slow warming to 25 °C (1 h) dichloromethane was added and the solution washed with aqueous sodium hydrogen carbonate and brine, dried, and evaporated. Chromatography on neutral alumina gave [eluant diethyl ether–light petroleum (1 : 19—1 : 9)] the benzyl ethers: 3β-benzyloxy-5α-cholestane (2c) (68—74%), m.p. 105—106 °C (from EtOH) (lit.,[2] 106—107 °C), $[\alpha]_D^{23}$ +17° (*c* 0.4) (lit.,[2] +15.1°); 3β-*benzyloxyergosta*-5,7,22-*triene* (3b) (63%), m.p. 129—131 °C (from $CH_2Cl_2$–MeOH), $[\alpha]_D^{25}$ −64° (*c* 0.5); $\nu_{max.}$ 1 600, 1 500, 1 455, 1 370, 1 360, 1 325, 1 255, 1 205, 1 195, 1 105, 1 025, 965, 845, 840, 725, and 690 $cm^{-1}$; $\lambda_{max.}$ (cyclohexane) 252sh (ε 4 500), 262sh (8 200), 275 (10 600), 281 (11 100), and 293 nm (6 300); δ 7.34 (5 H, s, aryl-H), 5.65—5.05 (4 H, m, 6-, 7-, 22-, 23-H), 4.57 (2 H, s, aryl-$CH_2$), and 3.65—2.95 (1 H, m, 3α-H); *m/e* 486 ($M^+$), 377, 363, 337, and 253 (Found: C, 86.2; H, 10.45. $C_{35}H_{50}O$ requires C, 86.35; H, 10.35%); 3-*O*-benzyl-1,2 : 5,6-di-*O*-isopropylidene-α-D-glucofuranose (4b) (64%) as an oil, $[\alpha]_D^{25}$ −26° (*c* 0.2 EtOH) (lit.,[3] −26.2); $\nu_{max.}$ 1 500, 1 455, 1 380, 1 370, 1 255, 1 215, 1 165, 1 120, 1 075, 1 025, 885, 850, 740, and 700 $cm^{-1}$; δ 7.23 (5 H, s, aryl-H), 5.83 (1 H, d, $J_{1,2}$ 3.5 Hz, 1-H), 4.59 (2 H, s, aryl-$CH_2$), 4.53 (1 H, d, 2-H), 4.47—3.8 (5 H, m), 1.47 (3 H, s), 1.40 (3 H, s), 1.35 (3 H, s), and 1.28 (3 H, s).

*Preparation of Methyl* 2,3-*Di*-O-*benzyl*-4,6,O-*benzylidene*-α-D-*glucopyranoside* (5b).—Methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (5a) (0.27 g, 1 mmol) and triethylamine (0.30 ml, 2 mmol) in THF (10 ml) were added to chlorobenzylidenedimethylammonium chloride (6a) [from *N,N*-dimethylbenzamide (0.40 g, 2.6 mmol)] in dichloromethane (10 ml). After being stirred overnight the initially red solution became yellow. The mixture was added to acetic acid-buffered sodium hydrogen telluride [from tellurium (0.87 g), sodium borohydride (0.60 g), and acetic acid (0.8 ml)] in ethanol (30 ml) at −20 °C. After 3 h at room temperature, work-up and chromatography on Merck Kieselgel 60 (13 g) gave (eluant light petroleum–diethyl ether–ethyl acetate gradient) methyl 2,3-*O*-dibenzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (5b) (97 mg, 27%), m.p. 97—99 °C (from light petroleum) (lit.,[4] 97.5—98.5 °C), $[\alpha]_D^{23}$ −30° (*c* 0.25) (lit.,[4] −31.0°); $\nu_{max.}$ 1 500, 1 465, 1 455, 1 370, 1 115, 1 090, 1 055, 1 030, 965, 745, 735, and 695 $cm^{-1}$; δ 7.6—7.1 (15 H, m, aryl-H), 5.56 (1 H, s, aryl-CH), 4.93, 4.78 (2 H, AB q, *J* 11.5 Hz, 2-C aryl-$CH_2$), 4.87 and 4.71 (2 H, AB q, *J* 12.5 Hz, 3-C aryl-$CH_2$), 4.61 (1 H, d, $J_{1,2}$ 3.5 Hz, 1-H), 4.35—3.2 (6 H, m), and 3.4 (3 H, s, OMe); *m/e* 462 ($M^+$) 431 and 371 (Found: C, 72.75; H, 6.6. Calc. for $C_{28}H_{30}O_6$ C, 72.7; H, 6.55%); methyl-2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (5c) (89 mg, 25%), m.p. 130—131.5 °C (from diethyl ether–light petroleum) (lit.,[4] 129.5 °C), $[\alpha]_D^{23}$ +33° (*c* 0.25) (lit.,[4] +4.0); $\nu_{max.}$ 3 465, 1 500, 1 455, 1 390, 1 385, 1 378, 1 360, 1 335, 1 315, 1 275, 1 215, 1 205, 1 200, 1 165, 1 150, 1 125, 1 105, 1 090, 1 080, 1 055, 1 030, 975, 965, 925, 750, and 700 $cm^{-1}$; δ 7.6—7.2 (10 H, m, aryl-H), 5.52 (1 H, s, aryl-CH), 4.80, 4.70 (2 H, AB q, *J* 12 Hz, 2-C aryl-$CH_2$), 4.60 (1 H, d, $J_{1,2}$ 3.5 Hz, 1-H), 4.35—3.2 (6 H, m), 3.36 (3 H, s, OMe), and 2.56 (1 H, d, *J* 2.5 Hz, OH); *m/e* 372 ($M^+$) 234, 193, and 163; and methyl 3-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (5d) (67 mg, 19%), m.p. 186—187 °C (from diethyl ether–light petroleum) (lit.,[4] 185—186 °C) $[\alpha]_D^{23}$ +78° (*c* 0.25) (lit.[4] +84.0°); $\nu_{max.}$ 3 300, 1 500, 1 455, 1 370, 1 140, 1 095, 1 075, 1 060, 1 030, 995, 750, 735, and 695 $cm^{-1}$; δ 7.55—7.05 (10 H, m), 5.52 (1 H, s, aryl-CH), 4.92, 4.75 (2 H, AB q, *J* 12 Hz, 3-C aryl-$CH_2$), 4.77 (1 H, d, $J_{1,2}$ 3.5 Hz, 1-H), 4.45—3.35 (6 H, m), 3.4 (3 H, s, OMe), and 2.3 (1 H, d, *J* 7 Hz, OH); *m/e* 372 ($M^+$) and 179.

*Preparation of Methyl* 4,6-O-*Benzylidene*-2,3-*di*-O-*benzoyl*-α-D-*glucopyranoside* (5g).—The diol (5a) (0.14 g, 0.5 mmol) and pyridine (0.40 ml, 5.0 mmol) in dichloromethane (10 ml) were added to chlorobenzylidenedimethylammonium chloride (6a) [from dimethylbenzamide (0.40 g, 2.5 mmol)] in dichloromethane (10 ml). After 1 h t.l.c. of a hydrolysed aliquot showed nothing less polar than the 3-benzoate (5f). Imidazole (0.34 g, 5.0 mmol) was added giving a white precipitate (1 min). This solid was, most reasonably, imidazole hydrochloride (n.m.r.). After 6 h 5% aqueous sodium hydrogen carbonate (20 ml) and dichloromethane were added. The organic phase was washed with aqueous sodium hydrogen carbonate and brine, dried, evaporated, and the residue chromatographed on neutral alumina (20 g). Elution with diethyl ether–light petroleum (1 : 9—3 : 17) gave the dibenzoate (5g) (174 mg, 73%), m.p. 152—154 °C (from dichloromethane–methanol) (lit.,[6] 154°), $[\alpha]_D^{21}$ +91° (*c* 0.336) (lit.,[6] +94 ± 2°).

The reaction was repeated. After the addition of imidazole the precipitate was filtered off ($N_2$) and the filtrate and washings ($CH_2Cl_2$) added to sodium hydrogen telluride [from tellurium (1.27 g, 10 mg-atom), sodium borohydride (0.74 g, 20 mmol), and acetic acid (1.20 ml, 20 mmol)] in ethanol (40 ml) at −20 °C. The mixture was warmed

up to room temperature (1 h) and quenched with aqueous sodium hydrogen carbonate. Work-up and repeated chromatography on alumina gave the dibenzyl ether (5b) (64 mg, 28%), 2-benzyl ether (5c) (20 mg, 11%), and 3-benzyl ether (5d) (20 mg, 11%), all identical with previous samples.

*Preparation of Methyl* 4,6-O-*Benzylidene*-2,3-*di*-O-*thiobenzoyl*-α-D-*glucopyranoside* (5i).—*N*-Benzoylpyrrolidine (0.25 ml, 1.5 mmol) in phosgene and dichloromethane (10% w/v; 10 ml) were allowed to react overnight. After evaporation the residue was redissolved in dichloromethane (10 ml). The diol (5a) (0.14 g, 0.5 mmol) and pyridine (0.20 ml, 2.5 mmol) in dichloromethane (10 ml) were added. After 1 and 6 h, respectively, imidazole (0.20 g, 3 mmol) and pyridine (0.30 ml) were added. Hydrogen sulphide was bubbled through the mixture for 15 min. Work-up of the yellow solution, removal of pyridine by its azeotrope with toluene, and chromatography on neutral alumina (50 g) gave [eluant diethyl ether–light petroleum (1 : 19)] methyl 4,6-*O*-benzylidene-2,3-di-*O*-thiobenzoyl-α-D-glucopyranoside (5i) (169 mg, 61%) as a foam identical (i.r., n.m.r., u.v.) with authentic material.[1] In addition two minor more-polar components (6 mg each) were isolated.

*Attempted Preparation of Methyl* 4,6-O-*Benzylidene*-2,3-*di*-O-*selenobenzoyl*-α-D-*glucopyranoside* (5j).—*N*,*N*-Dimethylbenzamide (0.23 g, 1.5 mmol) was converted into the imidoyl chloride (6a) in the usual way. To this in dichloromethane (10 ml) were added the diol (5a) (0.14 g, 0.5 mmol) and pyridine (0.20 ml, 2.5 mmol) in dichloromethane (10 ml). After 1 h imidazole (0.20 g, 3.0 mmol) was added. After 8 h the mixture was added to sodium hydrogen selenide [1] [from selenium (0.16 g, 2.0 mg-atom) and sodium borohydride (95 mg, 2.5 mmol)] in ethanol (20 ml) buffered with acetic acid (0.12 ml, 2.0 mmol) at 0 °C. After 45 min work-up and chromatography on neutral alumina (40 g) and Kieselgel 60 (15 g) gave [eluant diethyl ether–light petroleum (1 : 9)] an impure red glass, possibly the bis-selenobenzoate (5j) (21 mg, 7%); $\nu_{max.}$ 1 595, 1 450, 1 380, 1 315, 1 260, 1 190, 1 115, 1 095, 1 075, 1 050, 1 025, 990, 925, 765, 695, and 680 cm$^{-1}$; δ 8.3—7.9 (4 H, m, aryl-H), 7.8—7.0 (12 H, m, aryl-H + 3-H), 6.48 (1 H, dd, $J_{1,2}$ 4 Hz, $J_{2,3}$ 9.5 Hz, 2-H), 5.56 (1 H, s, aryl-CH), 5.38 (1 H, d, $J_{1,2}$ 4 Hz, 1-H), and 3.44 (3 H, s, OMe); and *methyl* 2-O-*benzoyl*-4,6-O-*benzylidene*-3-O-*selenobenzoyl*-α-D-*glucopyranoside* (5k) (59 mg, 21%) as red needles, m.p. 156—157.5 °C (from diethyl ether–light petroleum), $[\alpha]_D^{23}$ −83°, $[\alpha]_{578}^{23}$ −110° $\nu_{max.}$ 1 725, 1 450, 1 375, 1 270, 1 225, 1 210, 1 180, 1 170, 1 145, 1 105, 1 095, 1 070, 1 050, 1 025, 1 000, 950, 915, 775, 755, 715, and 700 cm$^{-1}$; $\lambda_{max.}$ (EtOH) 228 (ε 10 500), 256 (4 300), and 332 nm (4 100); δ 8.25—7.90 (4 H, m, aryl-H), 7.8—7.1 (12 H, m, aryl-H, 3-H), 5.58 (1 H, s, aryl-CH), 5.50 (1 H, dd, $J_{1,2}$ 4 Hz, $J_{2,3}$ 10.5 Hz, 2-H), 5.21 (1 H, d, $J_{1,2}$ 4 Hz, 1-H), 4.6—3.6 (4 H, m), and 3.46 (3 H, s, OMe); *m/e* 556, 554, 552 ($M^+$), 458, 369, 263, 149, and 105 (Found: C, 61.05; H, 4.8. $C_{28}H_{26}O_7Se$ requires C, 60.75; H, 4.75%). Reaction of methyl 4,6-*O*-benzylidene-3-*O*-selenobenzoyl-α-D-glucopyranoside (5l) with benzoyl chloride and pyridine gave the same product (5k).

*Reduction of* 1-(5α-*Cholestan*-3β-*yl*)-1-*phenylmethylenedimethylammonium Chloride* (2b).—(a) Tellurium (0.38 g, 3.0 mg-atom) and 18-crown-6 (0.58 g, 3.0 mmol) were added to potassium (0.24 g, 6.0 mg-atom) in DME (*ca.* 20 ml). Both elements dissolved in 1 h. After a further 1.5 h deoxygenated acetic acid (0.18 ml, 3.0 mmol) was added at −20 °C. Freshly prepared solvent-free imidate salt (2b) [from *N*,*N*-dimethylbenzamide (0.23 g, 1.5 mmol) and 5α-cholestan-3β-ol (2a) (0.39 g, 1.0 mmol)] redissolved in DME and ethanol (1 : 1; 10 ml) was added. Tellurium only deposited as the mixture warmed up to room temperature. After overnight stirring precipitation ceased, leaving a colourless solution. Work-up gave a complex mixture (t.l.c.). Although chromatographic separation was unsuccessful, some impure fractions gave a solid on trituration with dichloromethane–methanol. The solid (152 mg, 32%) was repeatedly recrystallised from chloroform–methanol to give αα′-*bis*-(5α-*cholestan*-3β-*yloxy*)*bibenzyl* (2d) as needles, m.p. 265—270°, $[\alpha]_D^{21}$ +15° (*c* 0.25); $\nu_{max.}$ 1 465, 1 450, 1 380, 1 365, 1 350, 1 085, 1 065, 1 025, 735, 720, and 700 cm$^{-1}$; δ 7.5—6.9 (10 H, m, aryl-H), 4.49—4.30 (2 H, 2s, aryl-CH), and 3.45—2.8 (2 H, m, 3α-H); *m/e* $M^+$ absent, 566, 492, 477, 388, 371, and 355 (Found: C, 85.55; H, 11.15. $C_{68}H_{106}O_2$ requires C, 85.45; H, 11.2%).

(b) Potassium (0.78 g, 20 mg-atom), tellurium (1.27 g, 10 mg-atom), and 18-crown-6 (2.12 g, 8.0 mmol; added in two portions) were stirred together in DME (*ca.* 40 ml). When the solids dissolved the solution was cooled to −25 °C and acetic acid (0.6 ml, 10 mmol) added to give a purple solution. *N*,*N*-Dimethylbenzamide (0.23 g, 1.5 mmol) in phosgene and benzene [10% (w/v); 10 ml] was added and allowed to react overnight; the mixture was then evaporated. To the residue in benzene (10 ml) was added 5α-cholestan-3β-ol (2a) (0.39 g, 1.0 mmol) in benzene. After 1.5 h the imidate salt (2b) was added as a suspension to the telluride solution at −25 °C. After stirring overnight at room temperature tellurium was deposited to leave a red solution. Work-up and p.l.c. [diethyl ether–light petroleum (3 : 17)] gave the dimer (2d) (65 mg, 12%) and benzyl ether (2c) (362 mg, 74%) identical (t.l.c., n.m.r.) with authentic materials.

*Preparation of the Borane Complex* (1i) (*with Dr. K. Picker*).—*N*,*N*-Dimethylformamide (0.55 g, 10 mmol) was added dropwise to phosgene in dichloromethane [20% (w/v); 10 ml]. After 30 min the mixture was evaporated and the residue dissolved in dichloromethane (20 ml) at −20 °C. Pre-chilled cholesterol (1h) (1.90 g, 5 mmol) in dichloromethane (10 ml) and THF (10 ml) was added during 15 min, the temperature being maintained at −20 °C, Triethylamine (1.5 g, 15 mmol) and, after 15 min, sodium borohydride (1.0 g, 27 mmol) in ethanol (20 ml) were added. The slurry was allowed to warm to room temperature during 1 h. The mixture was diluted with water, extracted with diethyl ether, and the organic phase dried and evaporated. Chromatography on neutral alumina (100 g) gave [eluant diethyl ether–light petroleum (1 : 4)] the *borane complex* (1i) (1.55 g, 72%), m.p. 155—158 °C (from acetone), $[\alpha]_D^{20}$ −31.2° (*c* 0.5); $\nu_{max.}$ 2 360, 2 270, 1 670, 1 605, 1 460, 1 370, 1 165, 1 100, 990, and 950 cm$^{-1}$; $\lambda_{max.}$ transparent >220 nm; δ 5.30 (1 H, m, 6-H), 5.0—3.0 (~6 H, m with s at 4.12, $OCH_2$, 3α-H $BH_3$ ?), and 2.57 (6 H, s, $NMe_2$); *m/e* $M^+$ absent, 415, 386, 368, 355, and 353 (Found: C, 78.8; H, 12.5; N, 3.0. $C_{30}H_{56}BNO$ requires C, 78.75; H, 12.35; N, 3.05%). The borane (1i) (30 mg) was dissolved in dichloromethane (10 ml) saturated with hydrogen chloride and the solution set aside overnight. The mixture was then evaporated and the residue crystallised from dichloromethane–light petroleum to give the *borane salt* (1j), m.p. 155—157 °C (decomp.), $[\alpha]_D^{21}$ −37° (*c* 0.25); $\nu_{max.}$ 2 445, 2 420, 1 210, 1 180, 1 105, 1 100, 1 035, 970, 840, and 810 cm$^{-1}$; δ 5.3 (1 H, m, 6-H), 4.25 (2 H, s, $OCH_2$), and 2.56 (6 H, s, $NMe_2$) (Found: C, 73.15; H, 11.6; Cl, 7.35; N,

2.85. $C_{30}H_{57}BClNO$ requires C, 72.95; H, 11.65; Cl, 7.2; N, 2.85%).

*Reaction of the Imidate Salt* (1b) *with Sodium Borohydride.*—Sodium borohydride (1.0 g) in ethanol (40 ml) was added slowly to the imidate (1b) [from cholesterol (1h) (3.8 g) and *N,N*-dimethylbenzamide (1.55 g)] in dichloromethane (15 ml) at −20 °C. After 30 min at −20 °C and 2 h warming to room temperature, water and diethyl ether were added. The organic phase was dried and evaporated to leave an oily solid (4.96 g). The products in diethyl ether were washed with 3M-hydrochloric acid. The aqueous layer was basified (NaOH) and re-extracted with diethyl ether; the organic phase was washed with brine, dried, and evaporated to leave *N,N*-dimethylbenzylamine identical (t.l.c., n.m.r., b.p.) with authentic material. Evaporation of the organic layer (acidic extraction) gave crude cholesterol (1h) (n.m.r., t.l.c.).

*Reaction of the Imidate Salt* (1d) *with Ethane-1,2-dithiol.*—Freshly distilled ethane-1,2-dithiol (0.9 ml) was added dropwise to the imidate salt (1d) [from DMF (0.55 g), triethylamine (1.5 ml), and cholesterol (1h) (1.98 g)] at −20 °C in dichloromethane (20 ml) and THF (10 ml). After 140 min the solution reached 10 °C and more ethane-1,2-dithiol (1.35 ml) was added. After being stirred overnight at room temperature the mixture was partitioned between dichloromethane and water. The organic phase was dried and evaporated; the residue gave cholesterol (1h) (1.32, 0.165 g) from acetonitrile (1st crop) and diethyl ether–methanol (2nd crop). The residue (0.93 g) was chromatographed on neutral alumina (eluant dichloromethane–light petroleum gradient) to give crude 2-(*N,N*-dimethylamino)-1,3-dithiolan (7) (0.6 g, 54%) identical with authentic material.

*Preparation of* 2-(N,N-*Dimethylamino*)-1,3-*dithiolan* (7).—DMF (5.0 g) was added to phosgene (30 g) in dichloromethane (60 ml). After 30 min the solvent was evaporated and to the residue in dichloromethane (40 ml) was added triethylamine (15 ml) and ethane-1,2-dithiol (10 ml) in rapid succession. After 1 h the mixture was washed with water, dried, evaporated, and repeatedly (with considerable loss) fractionally distilled to give 2-(N,N-*dimethylamino*)-1,3-*dithiolan* (7), b.p. 63 °C at 1 mmHg; $\nu_{max.}$ 2 970, 2 940, 2 930, 1 475, 1 455, 1 440, 1 425, 1 348, 1 270, 1 175, 1 153, 1 050, 1 025, 860, 845, 775, and 685 $cm^{-1}$; δ 6.16 (1 H, s), 3.13 (4 H, broad s), and 2.26 (6 H, s); *m/e* 149 ($M^+$), 121, 105, 89, and 60 (Found: C, 40.05; H, 7.6; N, 9.45. $C_5H_{11}NS_2$ requires C, 40.25; H, 7.45; N, 9.4%).

*Preparation of Cholest-5-en-3β-yl Benzimidate* (1p).—Finely divided ammonium chloride (21 g) and triethylamine (10 ml) were added in rapid sequence to the imidate salt (1b) [from cholesterol (1h) (7.7 g) and *N,N*-dimethylbenzamide (3.1 g)] in dichloromethane (20 ml) and THF (40 ml). After 30 min water was added, the mixture extracted with dichloromethane, and the organic phase dried and evaporated. Recrystallisation from diethyl ether–ethanol gave the *benzimidate* (1p) (5.53, 2.28, 1.19 g, 3 crops, 92%), m.p. 160—162 °C, $[\alpha]_D^{20}$ −22° (*c* 0.5); $\nu_{max.}$ 3 320, 1 630, 1 580, 1 340, 1 170, 1 060, 790, and 700 $cm^{-1}$; $\lambda_{max.}$ (cyclohexane) 225 (ε 8 060), 271 (440), and 279 nm (310); δ 7.8—7.1 (5 H, m, aryl-H), 7.1—6.2 (1 H, m, NH), 5.35 (1 H, m, 6-H), and 4.75 (1 H, m, 3α-H); *m/e* 489 ($M^+$), 386, and 368 (Found: C, 83.45; H, 10.6; N, 2.85. $C_{34}H_{51}NO$ requires C, 83.4; H, 10.5; N, 2.85%).

*Preparation of* 5α-*Cholestan*-3β-*yl Benzimidate* (2g).—The imidate salt (2b), ammonium chloride, and triethylamine gave 5α-*cholestan*-3β-*yl benzimidate* (2g) (83%), m.p. 141—142 °C, $[\alpha]_D^{21}$ +14° (*c* 0.7), $\nu_{max.}$ 3 300, 1 640, 1 630, 1 600, 1 580, 1 345, 1 175, 1 075, 783, and 698 $cm^{-1}$; $\lambda_{max.}$ (cyclohexane) 225 (ε 7 600), 271sh (380), and 279sh nm (230); δ 7.8—7.2 (5 H, m, aryl-H), 6.9—6.3 (1 H, m, NH), and 4.9 (1 H, 3α-H); *m/e* 491 ($M^+$), 388, and 370 (Found: C, 83.35; H, 11.1; N, 2.75. $C_{34}H_{53}NO$ requires C, 83.05; H, 10.85; N, 2.85%).

*Preparation of Cholest-5-en-3β-yl* N-*Toluene-4-sulphonylbenzimidate* (1q).—The imino-ether (1p) (245 mg, 0.5 mmol), toluene-4-sulphonyl chloride (0.10 g, 0.55 mmol), and pyridine (2 ml) were stirred for 4 days and then additional toluene-4-sulphonyl chloride (0.10 g) was added to the mixture. After 2 weeks the mixture was partitioned between water and dichloromethane. The organic phase was dried and evaporated and the residue crystallised from chloroform–methanol to give the *benzimidate* (1q) (crude product 0.32 g, *ca.* 100%), m.p. 134—136 °C, $[\alpha]_D^{20}$ −43° (*c* 0.512); $\nu_{max.}$ 1 590, 1 570, 1 490, 1 312, 1 300, 1 285, 1 154, 1 090, 975, 818, 800, 780, 744, 720, 705, and 688 $cm^{-1}$; $\lambda_{max.}$ (cyclohexane) 234 nm (ε 8 000); δ 7.8—7.0 (9 H, m, aryl-H), 5.2 (1 H, m, 6-H), 4.7br (1 H, m, 3α-H), and 2.4 (3 H, s, aryl-Me); *m/e*; $M^+$ absent, 487 and 368 (Found: C, 76.7; H, 8.9; N, 2.2. $C_{41}H_{57}NO_3S$ requires C, 76.45; H, 8.95; N, 2.2%).

*Attempted Preparation of Cholest-5-en-3β-yl* N-*Trifluoroacetylbenzimidate* (1s).—The iminoether (1p) (245 mg) in dichloromethane (2.5 ml) was cooled to −60 °C and triethylamine (80 μl) and trifluoroacetic anhydride (120 μl) were added. After 1 h the mixture reached room temperature, and water and dichloromethane were added. The organic phase was washed with water and brine, dried, and evaporated to leave a crystalline solid, m.p. 110—117 °C, $[\alpha]_D^{20}$ −23° (*c*, 0.496) $\nu_{max.}$ 1 725, 1 640, 1 625, 1 320, 1 304, 1 215, 1 193, 1 155, 1 088, 1 030, 878, 780, 718, and 705 $cm^{-1}$; $\lambda_{max.}$ (cyclohexane) 236 nm (ε 10 600); *m/e* 585 ($M^+$), 482, 467, 386, 368, and 353. Attempted recrystallisation resulted in decomposition.

*Reaction of the Benzimidate* (1s) *with Sodium Hydrogen Telluride.*—To the benzimidate (1p) (0.245 g) and imidazole (35 mg) in THF (2.5 ml) at 0 °C was added trifluoroacetic anhydride (100 μl). After 1 h, work-up gave the benzimidate (1s) identical with that described above. This in dichloromethane (2 ml) was added to sodium hydrogen telluride [from tellurium (90 mg), sodium borohydride (60 mg), and acetic acid (90 μl)] in ethanol (2 ml) at −20 °C under argon. After 2 h at room temperature work-up gave a yellow gum (0.32 g). P.l.c. on silica [developing solvent diethyl ether–light petroleum (1 : 19)] gave the benzoate (1t) (31 mg, 13%) (identical, t.l.c., i.r., u.v., and mass spectrum, with authentic material), and a solid (54 mg). Sublimation at 20 mmHg gave the carbinolamine derivative (8) identical with authentic material.

*Preparation of* α-*Ethoxy*-α-*trifluoroacetamidotoluene* (8).—Trifluoroacetic anhydride (0.50 ml) was added to ethyl benzimidate (0.50 g) and imidazole (0.23 g) in THF (3 ml) at 0 °C. After 30 min the mixture was filtered into sodium borohydride (0.25 g) in ethanol (5 ml). After 1 h the mixture in diethyl ether was washed with water, dried, and evaporated to leave a solid (0.614 g). Sublimation twice at 50 °C and 0.5 mmHg gave α-*ethoxy*-α-*trifluoroacetamidotoluene* (8) (0.389 g, 47%). Three recrystallisations from aqueous ethanol in the cold gave analytical material with m.p. 92—92.5 °C; $\nu_{max.}$ 3 360, 3 070, 1 705, 1 540, 1 410, 1 348, 1 210, 1 200, 1 185, 1 163, 1 105, 1 075, 1 025,

915, 880, 835, 752, 725, and 700 $cm^{-1}$; δ 7.4 (5 H, s, Ph), 6.6 (1 H, m, NH), 6.2 (1 H, d, *J* 9.5 Hz, NHC*H*), 3.7 and 3.67 (2 H, 2 q, *J* 7 Hz, $OCH_2$), and 1.28 (3 H, t, *J* 7 Hz, $CH_3$); *m/e* 247 ($M^+$), 218, 202 (100%), 135, 105, 79, and 77 (Found: C, 53.5; H, 4.9; N, 5.65. $C_{11}H_{12}F_3NO_2$ requires C, 53.45; H, 4.9; N, 5.65%).

*Preparation of Cholest-5-en-3β-yl* N-*Trifluoromethanesulphonylbenzimidate* (1r).—To the iminoether (1p) (245 mg) in dichloromethane (2.5 ml) at −78 °C was added triethylamine (80 μl) and trifluoromethanesulphonic anhydride (145 μl). After being allowed to warm up to 0 °C the mixture was diluted with dichloromethane and water. The organic phase was washed with water and brine, dried, and evaporated. Crystallisation from chloroform–methanol gave the *benzimidate derivative* (1r) as prisms, m.p. 120—147 °C with bulk 145—147 °C. Recrystallisation gave material with m.p. 147—150 °C, $[\alpha]_D^{20}$ −22.4° (*c* 0.535); $\nu_{max.}$ 1 590, 1 564, 1 370, 1 330, 1 290, 1 220, 1 198, 1 125, 718, 708, and 688 $cm^{-1}$; $\lambda_{max.}$ (cyclohexane) 246 nm (ε 6 300); δ 8.0 (2 H, dd, *J* 8 and 2 Hz, aryl-H), 7.63 (3 H, m, aryl-H), 5.55 (1 H, m, 6-H), 4.98 (1 H, m, 3α-H), 2.6 (2 H, m, 4α-, 4β-H), 0.90 (3 H, s, 10-Me), and 0.70 (3 H, s, 13-Me) (Found: C, 67.5; H, 8.1; N, 2.1. $C_{35}H_{50}F_3NO_3S$ requires C, 67.6; H, 8.1; N, 2.25%).

*Reaction of 5α-Cholestan-3β-yl Benzimidate* (2g) *with Iodine.*—The imino-ether (2g) (0.12 g) and iodine (0.62 g) were refluxed in benzene (20 ml). After 2 h the mixture in diethyl ether was washed with water, aqueous sodium metabisulphite, water, and brine, dried, and evaporated. P.l.c. (light petroleum) and crystallisation from acetonitrile gave 3α-iodo-5α-cholestane (46 mg, 37%), m.p. 109—111 °C, mixed m.p. with authentic material 105—112 °C; mixed m.p. with authentic 3β-iodo-5α-cholestane 72—100°.

*Preparation of 5α-Cholestan-3β-yl Benzohydrazonate* (2k).—Hydrazinium chloride (20 g, 20 equiv.) and triethylamine (5 ml) were added in rapid sequence to the imidate salt (2b) [from *N,N*-dimethylbenzamide (1.55 g) and 5α-cholestanol (2a) (3.88 g)] in THF (20 ml) and dichloromethane (20 ml). After being vigorously stirred for 30 min the mixture was partitioned between dichloromethane and aqueous potassium carbonate and then water. The organic extract was dried and evaporated to yield a red semi-solid (4.6 g). Crystallisation from dichloromethane–ethanol gave N,N′-*bis*-[α-5α-*cholestan*-3β-*yloxy*)*benzylidene*]-*hydrazine* (2j) (0.64 g, 13%), m.p. 235—238°, $[\alpha]_D^{22}$ −19° (*c* 0.781); $\nu_{max.}$ 1 610, 1 590, 1 570, 1 330, 1 280, 1 150, 1 120, 1 027, 774, and 694 $cm^{-1}$; δ 7.9, 7.5 (10 H, m, aryl-H), 5.7—4.9 (2 H, m, 3α-H, 3α′-H), and 0.7 (6 H, s, 13-Me, 13′-Me); *m/e* 980 ($M^+$), 860, 755, 492, 388, 370, 355, and 215 (Found: C, 83.15; H, 10.7; N, 2.85. $C_{68}H_{104}N_2O_2$ requires C, 83.2; H, 10.75; N, 2.85%). The mother-liquor gave 5α-*cholestan*-3β-*yl benzohydrazonate* (2k) (1.18 g, 23%), m.p. 148—154 °C from benzene–light petroleum. Recrystallisation twice from benzene–light petroleum gave analytical material, m.p. 153—155 °C, $[\alpha]_D^{20}$ +14° (*c* 0.25); $\nu_{max.}$ 3 400, 3 360, 1 620, 1 588, 1 335, 1 272, 1 110, 1 070, 1 022, 770, and 695 $cm^{-1}$; $\lambda_{max.}$ 267 nm (ε 7 300); δ 7.7—7.2 (5 H, m, aryl-H), 5.35 (2 H, m, $NH_2$), and 4.3—3.7 (1 H, m, 3α-H); *m/e* 506 ($M^+$), 371, and 136 (Found: C, 80.7; H, 10.85; N, 5.55. $C_{34}H_{54}N_2O$ requires C, 80.55; H, 10.75; N, 5.55%). The final mother-liquor became dark red after one week. Chromatography on Kieselgel H (13g) gave (eluant diethyl ether–light petroleum gradient) (*a*) minor gum, (*b*) 5α-cholestan-3β-yl benzoate (2n) (0.52 g, 11%), (*c*) a minor purple solid, (*d*) a complex oil (0.83 g), (*e*) 5α-cholestan-3β-ol (2a) (0.33 g, 8%), and (*f*) crude *N,N*-dimethylbenzamide (0.20 g). The purple fraction gave 3,6-diphenyl-1,2,4,5-tetrazine (9), m.p. 197—198 °C from dichloromethane–light petroleum) (lit.,[11] 194 °C); $\nu_{max.}$ 1 600, 1 390, 1 102, 930, 918, 772, 767, and 690 $cm^{-1}$; $\lambda_{max.}$ (EtOH) 294 nm (ε 21 000); δ 8.8 (4 H, dd, *J* 7, 2 Hz) and 7.77 (6 H, m); *m/e* 234 ($M^+$) and 103 (Found: C, 71.55; H, 4.3; N, 23.9. Calc. for $C_1H_{10}N$: C, 71.715; H, 4.3; N, 23.9%). A subsequent preparation gave the dimer (2j) (54%) and benzohydrazone (2k) (14%). The red mother-liquors (1.42 g), acetic anhydride (3 ml), and pyridine (2 ml) were stirred overnight and for 30 min at 100 °C. After dilution with dichloromethane the solution was washed with 5M-hydrochloric acid, water, aqueous sodium hydrogencarbonate, and water, dried, and evaporated. Chromatography on Kieselgel 60 (eluant diethyl ether–light petroleum gradient) gave (*a*) an inhomogeneous fraction, (*b*) impure (purple) 5α-cholestan-3β-yl acetate (2l) (14%), (*c*) 5α-*cholestan*-3β-*yl* N,N-*diacetylbenzohydrazonate* (2m) (1%), m.p. 149—152 °C (from ethanol); $\nu_{max.}$ 1 720, 1 700, 1 628, 1 600, 1 335, 1 302, 1 218, 975, and 695 $cm^{-1}$; *m/e* 590 ($M^+$), 530, 490, 428, 388, 370, 355, and 178 (Found: C, 77.2; H, 9.95; N, 4.7. $C_{38}H_{58}N_2O_3$ requires C, 77.25; H, 9.9; N, 4.75%), and (*d*) a compound, m.p. 201—202 °C (from benzene) which was not investigated further.

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