Synthesis and Reactions of t-Butyltellurocarbonyloxyalkanes [1]

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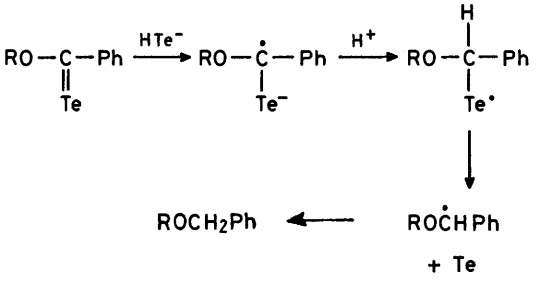
Reaction of t-butylchloromethylenedimethylammonium chloride with alcohols and sodium hydrogen telluride gave t-butyltellurocarbonyloxyalkanes. 3β-t-Butyltellurocarbonyloxy-5α-cholestane [$Bu^tC(=Te)OR$] gave the ester (Bu^tCO_2R) with diphenylseleninic anhydride, and ethers (Bu^tCH_2OR) and [$(Bu^tCHOR)_2$] with sodium hydrogen telluride. The ethers were formed *via* the oligotelluride [$(Bu^tCHOR)_2Te_n$; n = 1—4] which with *N*-bromosuccinimide gave the imide [(Bu^tCHOR)-$N(COCH_2CH_2CO)$].

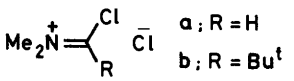
BENZYL ETHERS have been conveniently prepared by the reaction of alcohols with 1-chloro-1-phenylmethylenedimethylammonium chloride (1a) and sodium hydrogen telluride in sequence.[2] The reaction proceeds under mild conditions and therefore is applicable to the



SCHEME 1

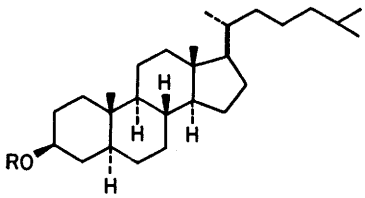
protection of hydroxy-groups in base-labile carbohydrate substrates. Most probably the transformation takes place *via* the tellurobenzoate and hydrogen atom transfer (Scheme 1). Consistent with this hypothesis we expected that alkyltellurocarbonyloxyalkanes (hereinafter 'telluroesters') should be isolable on account of decreased stabilisation of radical intermediates in the reductive loss of tellurium. In addition sterically hindered non-enolisable telluroesters should be more stable due to the suppression of polymerisation *etc.* Such compounds (telluropivatoates), which are stable when pure, have now been isolated.

N,*N*,2,2-Tetramethylpropionamide reacted with phosgene in dichloromethane to give the Vilsmeier salt t-butylchloromethylenedimethylammonium chloride (1b). After evaporation to remove excess of phosgene 5α-cholestan-3β-ol (2a) was added at −20 °C. At this stage hydrolysis of an aliquot gave 5α-cholestan-3β-yl pivaloate (2b), *vide infra*. Sodium hydrogen telluride (2.7 equiv.) buffered with acetic acid was added to give two products, neither of which was obtained in an homogeneous state; structural assignments are therefore tentative. The less-polar component was a telluriferous gum, the n.m.r. spectrum {δ 5.72—5.40 [1 H, m, Bu^tCH-(OR)Te], 3.81—3.1 (1 H, m, 3α-H), and 1.08 (9 H, s, Bu^t)} of which was consistent with its formulation as the oligotelluride mixture (2c). Microanalysis suggested the tellurium catenation was inhomogeneous. The more-polar homogeneous (t.l.c.) product (m.p. 120—126 °C, $[\alpha]_D$ +21°) had a microanalysis consistent with its formulation as $C_{32}H_{58}O$ and showed a parent ion in the mass spectrum at 458. With the exception of the n.m.r. data the spectral results were in accord with the product being 3β-(2,2-dimethylpropyloxy)-5α-cholestane (2d). The n.m.r. spectrum was, however, curious; the resonances at δ 4.06 (<1 H, s), 3.78 (1 H, m, 3α-H), and 3.42 (<2 H, m) being consistent with a mixture of the ether (2d) and pinacol diether (2e). The product, after microanalysis, on repeated recrystallisation gave a minor higher-melting solid, m.p. 187—191 °C.



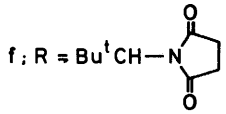
a; R = H
b; R = Bu^t

(1)



(2)

a; R = H
b; R = Bu^tCO
c; R = $(Bu^tCH)_2$—Te_n (n = 1—4)
d; R = Bu^tCH_2
e; R = $(Bu^tCH)_2$

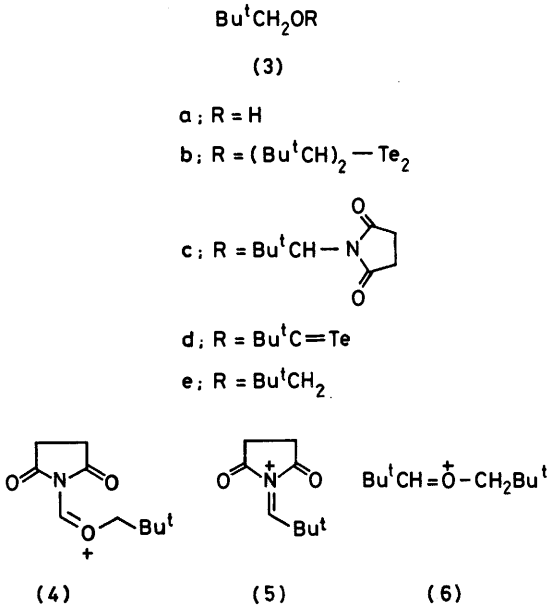


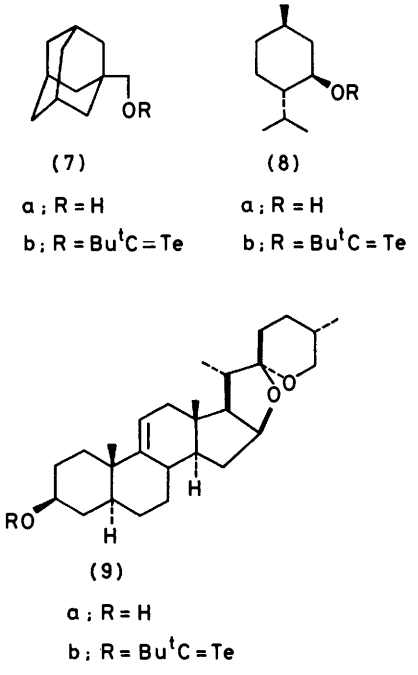
g; R = Bu^tC=Te
h; R = $Me_2\overset{+}{N}$=CBu^t Cl^-

The steroidal oligotelluride (2c) reacted with *N*-bromosuccinimide to give a stable crystalline solid ($C_{36}H_{61}NO_3$), with a double m.p. 138—140 and 160—165 °C, $[\alpha]_D^{23}$ +13°. Spectral data [*inter alia* $\nu_{max.}$ 1 785

and 1 705, δ 5.05 (1 H, s, Bu^tCH), 3.05 (1 H, m, 3α-H), 2.65 (4 H, s, $COCH_2CH_2CO$), and 0.97 (9 H, s, Bu^t)] were consistent with the imide (2f). Clearly this substantiated the formulation of the precursor as the oligotelluride (2c).

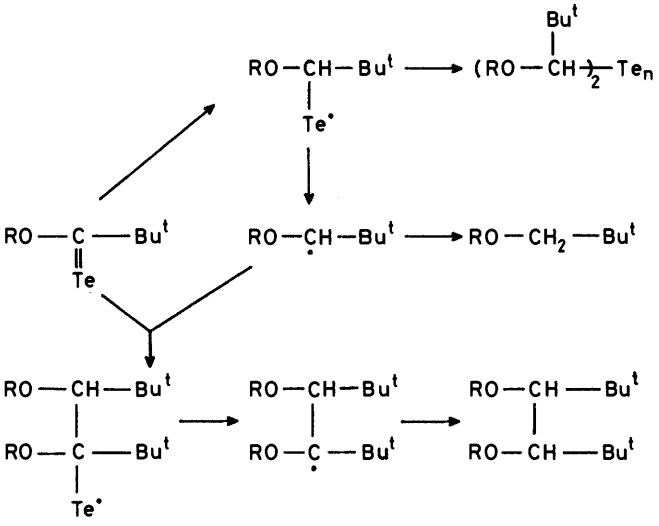
Analogously 2,2-dimethylpropan-1-ol (3a), t-butylchloromethylenedimethylammonium chloride (1b), and sodium hydrogen telluride gave a telluriferous com-





pound. Although this compound was not obtained pure the mass [574, 572, 570, 568, and 566 (M^+), and 157 (100%)] and n.m.r. spectra {δ 5.25 [2 H, s, Bu^tCH(OR)Te], 3.40, 2.75 (4 H, 2 AB q, J 8.5 Hz, Bu^tCH_2), 1.05 (18 H, s), and 0.93 (18 H, s)} were consistent with the formation of the ditelluride (3b) as a mixture of diastereoisomers. The product (3b) and *N*-bromosuccinimide gave a crystalline solid, m.p. 87—88 °C which, by analogy and on the basis of the spectral data, was formulated as the imide (3c); microanalyses were not, unfortunately, able to substantiate this. Fragments in the mass spectrum of the compound included ions at 256 $(M + H)^+$, 198 (4), 168 (5), and 157 (6).

The oligotelluride (2c) and ethers (2d) and (2e) were most probably formed *via* the telluropivaloate (2g) (Scheme 2), less sodium hydrogen telluride being



SCHEME 2

required. Reaction of 5α-cholestan-3β-ol (2a) (2.5 mmol), t-butylchloromethylenedimethylammonium chloride (1b) (2 mmol), and sodium hydrogen telluride (2 mmol) with vigorous exclusion of oxygen and subdued (red) lighting gave a product which upon rapid chromatography furnished violet needles of the pure compound (90%), m.p. 116—120 °C. The microanalysis and the mass spectrum [586, 584, 582, 581, 580, and 578 (M^+)] of the compound were consistent with its formulation as $C_{32}H_{56}OTe$; its u.v. spectrum [$\lambda_{max.}$ (cyclohexane) 243 (ε 4 300), 266sh (830), 346 (7 600), and 592 nm (320)] was especially informative. t-Butylselenocarbonyloxyethane absorbs at 274 (ε 7 950) and 450 nm (50).[3] The n.m.r. spectrum of the compound showed only one non-steroidal resonance, this (δ 1.28) being ascribed to the t-butyl group. Clearly the violet compound was 5α-cholestan-3β-yl telluropivaloate (2g).

A series of telluropivaloates (3d), (7b), (8b), and (9b) were prepared analogously all of which had satisfactory analyses apart from the menthol derivative (8b). The telluropivaloates (3d), (7b), and (8b) gave high-resolution mass ion measurements in excellent agreement with theory (^{130}Te). The most characteristic features of these compounds were (i) the u.v. spectra, (ii) the t-butyl signals at δ 1.27—1.37 in the ^1H n.m.r. spectra, and (iii) the tellurocarbonyl resonance at δ 229 in the ^{13}C n.m.r. spectra. When pure the telluropivaloates were stable, being unaffected by oxygen in the dark,

anaerobic photolysis (>500 nm) in benzene solution, and water.

5α-Cholestan-3β-yl telluropivaloate (2g) reacted with benzene–seleninic anhydride [4] with discharge of colour; chromatography gave 5α-cholestan-3β-yl pivaloate (2b) (96%), m.p. 164—166 °C identical with that from t-butyl-(5α-cholestan-3β-yloxy)methylenedimethylammonium chloride (2h) and water.

Nickel boride, prepared *in situ*,[5] and telluropivaloate (2g) gave a mixture of compounds including 3ε-chloro-5α-cholestane (t.l.c.), the ethers (2d) and (2e), the ester (2b) (n.m.r.), and 5α-cholestan-3β-ol (2a). Telluropivaloate (2g) and an excess of sodium hydrogen telluride gave, initially, the oligotelluride (2c) and finally the ethers (2d) and (2e). These results support the intermediacy of tellurobenzoates in benzylation using the Vilsmeier salt (1a) and sodium hydrogen telluride.

This work demonstrates that Vilsmeier methodology permits the synthesis of hitherto unavailable telluroesters; alternative telluroacylating reagents are unknown.*

EXPERIMENTAL

M.p.s were recorded on a Kofler hot-stage. I.r. spectra were recorded as Nujol mulls (solids) or liquid films. U.v. and n.m.r. spectra were recorded in cyclohexane and deuteriochloroform (tetramethylsilane reference) solutions respectively. Optical rotations refer to chloroform solutions; the rotations of the steroidal telluropivaloates (2g) and (9b) may not be reliable because of the chromophore at 592 nm. Light petroleum refers to the redistilled fraction b.p. 40—60 °C. Organic extracts were dried over anhydrous sodium sulphate.

Preparation of 3β-(2,2-*Dimethylpropyloxy*)-5α-*cholestane* (2d).—*N*,*N*,2,2-Tetramethylpropionamide (0.28 ml, 2.0 mmol) was treated with an excess of phosgene in dichloromethane (10% w/v; 10 ml). The reaction was followed by n.m.r. spectroscopy and shown to be complete within 1.5 h at room temperature. Solvent was removed and the residue dried thoroughly *in vacuo*, redissolved in dichloromethane (10 ml), and cooled to −20 °C. 5α-Cholestan-3β-ol (2a) (0.58 g, 1.5 mmol) in dichloromethane (10 ml) was added slowly and stirring continued between −15 and −10 °C for 3 h, after which time the reaction was complete (t.l.c.). Tellurium (0.51 g, 4.0 mg-atom) and sodium borohydride (0.30 g, 8.0 mmol) in ethanol (20 ml) were refluxed with stirring to effect dissolution (30—45 min); the mixture was then cooled to −20 °C, and acetic acid (0.50 ml, 8.0 mmol) added to act as a buffer. The solution of the imidate salt (2h) was added, the mixture allowed to warm up to room temperature (30 min), and saturated aqueous sodium hydrogen carbonate added. The organic phase was washed with brine, dried, and evaporated. Chromatography twice on neutral alumina gave (eluant light petroleum) the oligotelluride mixture (2c) as the major product (0.37 g) as a deep yellow gum, homogeneous by t.l.c.; $\nu_{max.}$ 1 465, 1 380, 1 365, 1 250, 1 175, 1 130, 1 065, 1 035, 1 015, 930, and 910 cm^{-1}; $\lambda_{max.}$ 263 (ε 7 700), 302sh (3 200), and 358sh nm (1 200); δ 5.72—5.40 [1 H, m, Bu^{t}C*H*(OR)Te], 3.8—3.1 (1 H, m, 3α-H), and 1.08 (9 H, s, Bu^t); *m/e* M^+ absent, 646, 644, 642, 640, 572, 570, 568, 516, 514, 512, 458, 406, and 371 (Found: C, 63.05; H, 9.55. $C_{64}H_{114}O_2Te_n$ requires C, 73.65; 65.65, 59.2, 53.9; H, 11.0, 9.8, 8.85, 8.05%; n = 1, 2, 3, and 4 respectively) and (eluant light petroleum) crude 3β-(2,2-*dimethylpropyloxy*)-5α-*cholestane* (2d) and (2e) (0.15 g, 22%), m.p. 120—126 °C (from acetone), $[\alpha]_D$ +21° (*c* 0.143); $\nu_{max.}$ 1 390, 1 120, and 1 055 cm^{-1}; δ 4.06 (<1 H, s), 3.78 (1 H, m, 3α-H), 3.42 (<2 H, m), 0.98 (9 H, s, Bu^t) 0.80 (3 H, s, 10-Me), and 0.64 (3 H, s, 13-Me); *m/e* 458 (M^+), 416, 388, 371, 355, and 316 (Found: C, 83.6; H, 12.75. $C_{32}H_{58}O$ requires C, 83.75; H, 12.75%). Further recrystallisation (after microanalysis) from diethyl ether–acetone gave a minor product, m.p. 187—191 °C.

Reaction of the Oligotelluride (2c) *with* N-*Bromosuccinimide*.—Solid *N*-bromosuccinimide (90 mg, 0.5 mmol) was added to the oligotelluride (2c) (0.246 g) in dry dichloromethane (10 ml) and the mixture was stirred overnight. The black suspension was filtered off and the residue washed with more dichloromethane. The combined filtrate and washings were evaporated and the residue chromatographed on neutral alumina (15 g). Diethyl ether–light petroleum (1 : 9 to 1 : 4) eluted N-[1-(5α-*cholestan*-3β-*yloxy*)-2,2-*dimethylpropyl*]*succinimide* (2f) (0.16 g, 68%) as colourless plates, double m.p. 138—140 and 160—165 °C (from dichloromethane–methanol), $[\alpha]_D^{23}$ +13.0° (*c* 0.4), $\nu_{max.}$ 1 785, 1 705, 1 465, 1 400, 1 380, 1 365, 1 340, 1 250, 1 220, 1 170, 1 145, 1 120, 1 095, 1 050, 935, 910, 820, and 760 cm^{-1}; δ 5.05 [1 H, s, Bu^{t}C*H*(OR)N], 3.05 (1 H, m, 3α-H), 2.65 (4 H, s, $COCH_2CH_2CO$), and 0.97 (9 H, s, Bu^t); *m/e* M^+ absent, 498 (weak), 371, 355, 316, 257, and 215 (Found: C, 77.65; H, 11.15; N, 2.5. $C_{36}H_{61}NO_3$ requires C, 77.75; H, 11.05; N, 2.5%).

Attempted Preparation of 2,2,6,6-*Tetramethyl*-4-*oxaheptane* (3e).—*N*,*N*,2,2-Tetramethylpropionamide (1.75 ml, 12.50 mmol) was treated with phosgene and dichloromethane (20% w/v; 20 ml) in the presence of pyridine (0.80 ml, 10.0 mmol). After 90 min, the reaction being complete, solvent was removed *in vacuo* and the residue redissolved in dichloromethane (20 ml). The solution was cooled to −10 °C and 2,2-dimethylpropan-1-ol (3a) (0.88 g, 10.0 mmol) added in dichloromethane (20 ml). The solution was maintained at −10 °C for 1.5 h (after which time n.m.r. spectroscopy showed complete reaction) and the mixture was added to a solution of sodium hydrogen telluride [prepared from tellurium (3.17 g; 25.0 mg-atom), sodium borohydride (1.85 g, 50.0 mmol), and acetic acid (3.0 ml; 50.0 mmol) in ethanol (50 ml)] at −20 °C. The dark mixture was allowed to warm to 10 °C during 1 h after which it was diluted with diethyl ether, washed with sodium hydrogen carbonate solution, water, and brine, and dried and evaporated under reduced pressure. The dark yellow oil was protected from light. Rapid chromatography on neutral alumina gave (eluant light petroleum) the ditelluride (3b) as a yellow oil (2.01 g, 72%), $\nu_{max.}$ 1 475, 1 460, 1 405, 1 390, 1 365, 1 320, 1 290, 1 265, 1 250, 1 215, 1 130, 1 080, 1 025, 1 015, 985, 935, 920, 895, 745, and 730 cm^{-1}; δ 5.25 [2 H, s, Bu^{t}C*H*(OR)], 3.40, 2.75 (4 H, 2 AB q, *J* 8.5 Hz, Bu^{t}CH_2OR), 1.05 [18 H, s, Bu^{t}CH(OR)Te], and 0.93 (18 H, s, Bu^t); *m/e* 574, 572, 570, 568, 566 (M^+), 530, 528, 526, 524, 522, 488, 486, 484, 482, 444, 402, 400, 398, 396, 260, 258, 256, 254, 158, 157 (100%), and 115.

Reaction of the Oligotelluride (3b) *with* N-*Bromosuccin-*

* Tellurocarbonyl derivatives of trisubstituted hydrazines have been prepared by Professor L. K. Henriksen (University of Copenhagen) (personal communication to D. H. R. B., July 13th, 1979).

imide.—To the oligotelluride (3b) (0.20 g) in dichloromethane (5 ml) was added *N*-bromosuccinimide (0.15 g) and the mixture was stirred overnight in the dark. The dark solid was filtered off and washed with dichloromethane and diethyl ether. The filtrate and washings were evaporated and redissolved in a little diethyl ether; a yellow gum was precipitated on the addition of light petroleum. Evaporation of the soluble fraction gave *N*-[2,2-dimethyl-1-(2,2-dimethylpropyloxy)]propylsuccinimide (3c) (0.12 g, 66%). Crystallisation from aqueous methanol gave colourless needles, m.p. 87—88 °C; $\nu_{max.}$ 1 780, 1 700, 1 480, 1 465, 1 400, 1 370, 1 360, 1 340, 1 300, 1 290, 1 250, 1 225, 1 180, 1 170, 1 165, 1 145, 1 120, 935, 900, 825, and 750 cm^{-1}; δ 4.9 [1 H, s, Bu^{t}C*H*(OR)N] 3.02, 2.88 (2 H, AB q, *J* 8.5 Hz, Bu^{t}CH_2O), 2.67 (4 H, s, $COCH_2CH_2CO$), 1.0 (9 H, s, *Bu*^{t}CH), and 0.91 (9 H, s, *Bu*^{t}CH_2); *m/e* 256 $(M + H)^+$, 198, 168, 157, 128, 100, and 71.

General Preparation of t-Butyltellurocarbonyloxyalkanes (2g), (3d), (7b), (8b), *and* (9b).—*N,N*,2,2-Tetramethylpropionamide (0.28 ml, 2.0 mmol) was treated for 90 min at room temperature with phosgene in dichloromethane (10% w/v; 10 ml) before solvent was removed *in vacuo* and the residue dried thoroughly. To a cooled solution of the residue in dichloromethane (10 ml) was added the alcohol (2a), (3a), (7a), (8a), or (9a) (2.5 mmol) in dichloromethane (10 ml) and the mixture stirred at this temperature until reaction was complete (by n.m.r. spectroscopy and/or t.l.c.; usually 0.5—1.5 h). From this point, all manipulations, including those involved in the working and purification processes, were performed *in subdued light*, often with the aid of a red photo-filtered lamp. Once the reaction was complete the solution was cooled to −78 °C and to it was slowly added *via* a double-tipped needle, under nitrogen, a solution of sodium hydrogen telluride [prepared from tellurium (0.254 g; 2.0 mg-atom) and sodium borohydride (0.152 g, 4.0 mmol) in ethanol (15 ml) and buffered with acetic acid (0.24 ml, 4.0 mmol) at −20 °C]. After 10—20 min the reaction was quenched at −78 °C by dropwise addition of sodium hydrogen carbonate solution and worked up by extraction of the product into diethyl ether. The ether solution was washed with brine, dried (Na_2SO_4), and evaporated at room temperature under reduced pressure. The highly coloured residue was rapidly filtered through a column of neutral alumina, in light petroleum, to remove excess of alcohol. This treatment gave the telluroester in a fairly pure state. To remove the oligotelluride and non-telluroester, usually present in minor amounts, extensive chromatography on Merck Kieselgel (type 60 H) was required with substantial loss of product as a result of decomposition. The following telluro-pivaloates were prepared by this method. The temperature of the reaction between the imidoyl chloride (1b) and the alcohol, and the reaction time are shown in parentheses. (a) 3β-*t-Butyltellurocarbonyloxy*-5α-*cholestane* (2 g) (90%) (−25 to −20 °C, 1—1.5 h) was obtained as violet needles, m.p. 116—120 °C (decomp.) (from acetone–light petroleum), $[\alpha]_{578}^{22}$ −44° (*c* 0.50); $\nu_{max.}$ 1 465, 1 375, 1 325, 1 250, 1 210, 1 195, 1 125, 1 045, 1 005, 985, 955, 920, 800, and 730 cm^{-1}; $\lambda_{max.}$ 243 (ε 4 300), 266sh (830), 346 (7 600), and 592 nm (320); δ 5.55 (1 H, m, 3α-H) and 1.28 (9 H, s, Bu^t); *m/e* 586, 584, 582, 581, 580, 578 (M^+), 472, 458, 370 (100%), 355, 316, and 257 (Found: C, 65.65; H, 9.7. $C_{32}H_{56}OTe$ requires C, 65.75; H, 9.65%). (b) *(1-t-Butyltellurocarbonyloxy)-2,2-dimethylpropane* (3d) (63%) (0 °C, 1 h) was obtained as a violet oil; ν_{max} 1 475, 1 460, 1 390, 1 365, 1 360, 1 275, 1 245, 1 230, 1 205, 1 190, 1 075, 1 055, 995, 960, 930, and 800 cm^{-1}; $\lambda_{max.}$ 243 (ε 3 100), 265 (850), 336 (5 900), and 584 nm (170); δ 4.2 (2 H, s, Bu^{t}CH_2O), 1.37 (9 H, s, Bu^{t}C=Te), and 1.1 (9 H, s, *Bu*^{t}CH_2-O); δ(^{13}C) 229.38 (s, C=Te), 94.61 (t, Bu^{t}CH_2O), 58.43 [s, $(CH_3)_3CC$=Te], 32.05 (s, $CH_3)_3CCH_2O$], 29.84 [q, $(CH_3)_3$CC=Te], and 26.68 [q, $(CH_3)_3CCH_2O$]; *m/e* 286, 284, 282, 281, 280, and 278 (M^+), 260, 258, 256, 254, 253, 252, 157 (100%), 87, 86, and 85 (Found: C, 42.45; H, 7.25%; M^+, 286.058 3. $C_{10}H_{20}OTe$ requires C, 42.3; H, 7.1%; M^+, 286.058 4). (c) 1-*t-Butyltellurocarbonyloxymethyladamantane* (7b) (91%) (0—20 °C, 30 min) was obtained as a low-melting violet solid; $\nu_{max.}$ 1 475, 1 450, 1 390, 1 375, 1 360, 1 320, 1 265, 1 255, 1 210, 1 185, 1 050, 1 005, 985, 975, 950, 935, and 800 cm^{-1}; $\lambda_{max.}$ 244 (ε 3 800), 266sh (800), 337 (8 400), and 596 nm (290); δ(^{1}H) 4.12 (2 H, s, CH_2-O), 2.25—1.55 (15 H, m), and 1.35 [9 H, s, Bu^{t}C(=Te)]; δ(^{13}C) 229.20 [*C*(=Te)], 94.96 (CH_2-O), 58.61 [$(CH_3)_3CC$(=Te)], 39.26 (adamantyl C-2), 36.71 (adamantyl C-4), 33.79 (Me_3C-CH_2-O), 29.94 [$(CH_3)_3$CC(=Te)−], and 27.75 (adamantyl C-3); *m/e* 364, 362, 360, 359, 358, 356 (M^+), 193, and 149 (100%) (Found: C, 53.15; H, 7.3%; M^+, 364.105 2. $C_{16}H_{26}OTe$ requires C, 53.1; H, 7.25%; M^+, 364.105 3). (d) 3β-(*t-Butyltellurocarbonyloxy*)-Δ^9-*tigogenin* (9b) (28%) [spirostanol (9a) added in tetrahydrofuran (THF) in place of dichloromethane; −15 to −10 °C, 1.5 h] was obtained as a violet solid, m.p. 160—165 °C (decomp.), $[\alpha]_{589}^{21}$ −33°, $[\alpha]_{578}^{21}$ −104° (*c* 0.5); $\nu_{max.}$ 1 460, 1 375, 1 270, 1 260, 1 250, 1 240, 1 210, 1 180, 1 155, 1 090, 1 065, 1 050, 990, 980, 960, 920, 895, 865, 820, 795, and 715 cm^{-1}; $\lambda_{max.}$ 243 (ε 3 700), 265sh (550) 346 (6 800), and 590 nm (240); δ 5.65 (1 H, m, 3α-H), 5.32 (1 H, m, 11-H), 4.65—4.15 (~1 H, m, 16α-H, contains impurity), 3.4 (2 H, m, 26-H$_2$), 1.3 (9 H, s, Bu^t), and 1.6, 1.04, 0.94, 0.85, and 0.70 (methyl peaks); *m/e* 612, 610, 608, 607, 606 (M^+), 434, 432, 397, 336, and 318 (Found: C, 63.1, 63.25; H, 8.6, 8.35. $C_{32}H_{50}O_3Te$ requires C, 62.95; H, 8.25%). (*e*) 1R,2S,5R-1-(*t-Butyltellurocarbonyloxy*)-2-*isopropyl*-5-*methylcyclohexane* (8b) (6%) (addition of triethylamine required for complete reaction; 0. to 10 °C 1 h) was obtained as a violet oil; $\nu_{max.}$ 1 475, 1 455, 1 390, 1 370, 1 355, 1 265, 1 255, 1 230, 1 210, 1 195, 1 150, 1 095, 1 040, 990, 945, 905, and 795 cm^{-1}; $\lambda_{max.}$ 241 (ε 3 500), 265 (620), 346 (6 600), and 589 nm (240); δ 6.0—5.3 (1 H, m, −CH_2O) and 1.27 [9 H, s, Bu^{t}C(=Te)−]; *m/e* 354, 352, 350, 349, 348, 346 (M^+), 149 (100%), 97, 83, 69, and 57 (Found: M^+, 354.121 5. $C_{15}H_{28}OTe$ requires M^+, 354.121 0).

Reactions of 3β-t-*Butyltellurocarbonyloxy*-5α-*cholestane* (2g). (a) *With diphenylseleninic anhydride*. To a solution of the telluroester (2g) (58 mg, 0.1 mmol) in dry THF (5 ml), under nitrogen in a vessel protected from light, was added diphenylseleninic anhydride (40 mg, 0.11 mmol). Tellurium was fairly rapidly deposited from the reaction mixture which, after being stirred for 1 h, showed (t.l.c.) complete disappearance of starting material. Most of the THF was evaporated under reduced pressure and the crude material separated by p.l.c. on silica [developed twice in diethyl ether–light petroleum (1 : 49)] to give diphenyl diselenide (32 mg, 92%) and 5α-*cholestan*-3β-*yl pivaloate* (2b) (45 mg, 96%). The ester was identical in all respects with a sample prepared from 5α-cholestan-3β-ol (2a) by condensation with the imidate salt (1b) followed by hydrolysis, m.p. 146—166 °C, $[\alpha]_D^{21}$ +14.3° (*c* 0.5); $\nu_{max.}$ 1 725, 1 285, 1 175, 1 132, 1 030, and 1 005 cm^{-1}; δ 5.7 (1 H, m, 3α-H), 1.3 (9 H, s, Bu^t), and 0.90, 0.80, and 0.67 (methyl

peaks); *m/e* 472 (M^+), 370 (100%), 355, and 215 (Found: C, 81.2; H, 12.0. $C_{32}H_{56}O_2$ requires C, 81.3; H, 11.95%).

(b) *With nickel boride.* The telluroester (2 g) (58 mg, 0.1 mmol) was dissolved with difficulty at room temperature in absolute ethanol (75 ml) with protection from light. To the solution was added nickel chloride hexahydrate (1.19 g, 5 mmol), with stirring, followed by boric acid (3.1 g, 50 mmol). Although difficult to ascertain, the purple colour of the telluroester appeared to be lost at this stage. After 5 min sodium borohydride (0.38 g, 10 mmol) in water (5 ml) was added dropwise. Stirring was continued at room temperature under nitrogen for 3 h. T.l.c. showed four products. After evaporation the residue in diethyl ether was washed with 5% aqueous sodium hydrogen carbonate, water, and brine, dried, and evaporated. P.l.c. on silica [2 developments in diethyl ether–light petroleum (3 : 97)] gave (in order of increasing polarity) a minor product co-chromatographing with 3α-chloro-5α-cholestane, a mixture of ethers (2d) and (2e), the ester (2b) (30 mg) (9 : 1 by n.m.r.), and 5α-cholestan-3β-ol (2a) (7 mg).

(c) *With excess of sodium hydrogen telluride.* Tellurium (0.254 g, 2.0 mg-atom) and sodium borohydride (0.52 g, 4.0 mmol) were refluxed together in ethanol (15 ml) under nitrogen. Once the tellurium had dissolved the colourless solution was cooled to −20 °C and buffered with glacial acetic acid (0.24 ml, 4.0 mmol). Within 5 min a solution of the telluroester (2g) (58 mg, 0.1 mmol) in dry dichloromethane (5 ml) was added and the mixture maintained below −10 °C for 1 h. The dark brown solution had deposited some tellurium and the mixture was slowly allowed to warm to room temperature. T.l.c. after 3 h showed mostly oligotelluride (2c) and 5α-cholestan-3β-ol (2a) (*ca.* 1 : 1) but no ester (2b) nor ethers (2d) or (2e). Stirring was continued under nitrogen for 4 days. After this time the ethers (2d) and (2e), 5α-cholestan-3β-ol (2a), and a yellow volatile telluriferous species [more polar than the oligotelluride (2c)] were detected. Work-up and p.l.c. on silica [diethyl ether–light petroleum (1 : 19)] gave the ethers (2d) and (2e) (26 mg, 57%) identical with those prepared previously (n.m.r.).

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