The Deoxygenation of *NN*-Dialkylaminothiocarbonyloxyalkanes

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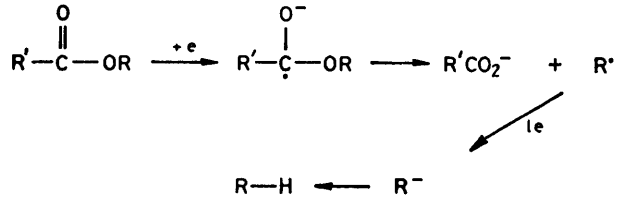
The title compounds were converted into alkanes in high yield on reduction with potassium and 18-crown-6 in t-butylamine. Thereby both primary and secondary alcohols were conveniently deoxygenated.

We have recently redefined ester reduction chemistry.[1] A dissolving Group 1A metal brings about alkyl–oxygen cleavage at the radical-anion stage giving rise to deoxygenation (Scheme 1). At room temperature in a nucleophile-free medium this is the principal reaction; the Bouveault–Blanc and acyloin reactions are curiosities.

Herein we report our studies on the reduction of carbonates, related sulphur compounds *etc.* Reduction was carried out using either lithium in ethylamine or potassium solubilised by 18-crown-6 in t-butylamine (see Table and Experimental section). We considered



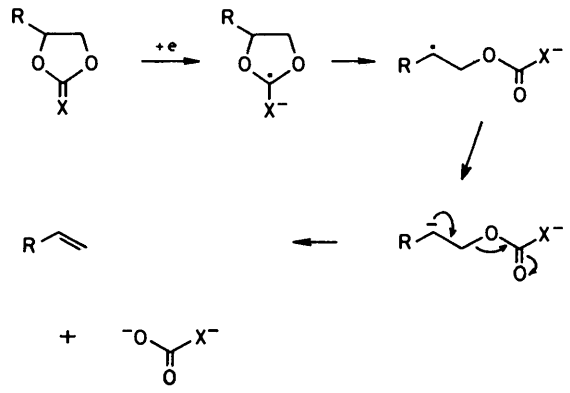
SCHEME 1

that xanthates (dithiocarbonates) and derived thiocarbamates should be highly suitable substrates for deoxygenation.[1] We anticipated that alkyl–oxygen cleavage of the derived radical anion would be favoured by formation of the stabilised sulphur anion (*e.g.* MeS·CO·S$^-$). In addition, nucleophilic displacement of xanthates by the amine solvent would afford thiocarbamates and the latter, if displaced, would reform the same functional group. Therefore, such derivatives should be relatively free from solvolytic complications.

The 1,3-dioxolan-2-one and -2-thione derivatives (1a,b) and (2a,b) were also reduced in the hope that the corresponding olefin would be formed (Scheme 2). In this way the important diol to olefin[2] transformation would be achieved. Several diverse compounds, toluene-4-sulphonate (3a), *O*-thioacetate (4a), imino-ether (4b), and epoxide (8) were also reduced.

The substrates in the Table were prepared by standard methods. Formation of derivatives of 5α-cholestane-3β,6β-diol (5f) were sometimes accompanied by elimination of the axial substituent and co-formation of the corresponding cholesterol derivative. Attempts to prepare the hindered dicarbonate (5k) or dicarbamate (5l) were unsuccessful; cholesterol (4d) (90%) and 3β-(*N*-piperidinocarbonyloxy)cholest-5-ene (4g) (75%) were formed. The preparation of the dixanthate (5c) presented a minor problem. Using the sodium hydride, carbon disulphide, iodomethane procedure[3] the principal product obtained was the monoxanthate-monothiocarbonate (5i). The dixanthate (5c) was prepared (53%) by the sequential reaction of 5α-cholestane-3β,6β-diol (5f) with n-butyl-lithium, carbon disulphide, and iodomethane.

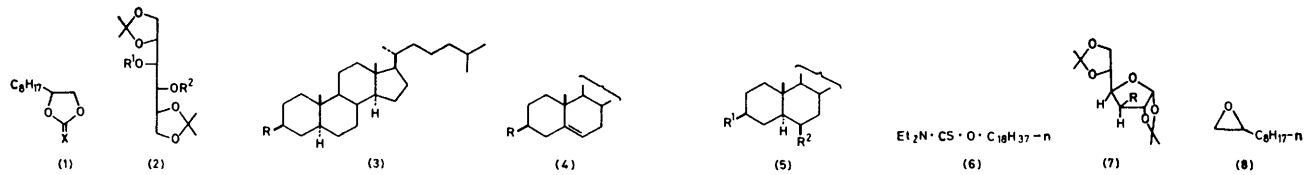
Reduction of the 1,3-dioxolan-2-one or -2-thione derivatives (Table, entries 1—4) were preparatively



SCHEME 2

unsatisfactory. However formation of more decan-1-ol than decan-2-ol from the thione (1b) was consistent with ring fragmentation at the radical-anion stage (Scheme 2). In general, with the exception of xanthates and thiocarbamates all the alcohol derivatives were not efficiently deoxygenated. However deoxygenation, when observed, was greatest at the most sterically hindered positions (entries 15 and 17).

In contrast, the reduction of the dixanthate (5c) and especially the dialkylaminothiocarbonyloxyalkanes (3d,e,f), (5e), and (6) proceeded with high overall deoxygenation. This deoxygenation is preparatively very attractive: the alcohol derivatives are readily available, work-up is easy, and even primary alcohols are readily removable. We note with interest that deoxygenation was suppressed at low temperature (entries 10 and 11). This, presumably, resulted from an increase in the lifetime of the radical anion. The bis-monoalkylaminothiocarbonyloxyalkane (5d) was not deoxygenated in high yield (entries 20 and 21). Clearly the alcohols must have arisen by alkoxide elimination from the conjugate base of (5d). The glucofuranose thiocarb-



(1) (2) (3) (4) (5) (6) (7) (8)

(1): a; X = O; b; X = S

(2): a; R^1,R^2 = CO; b; R^1,R^2 = CS; c; R^1 = R^2 = $Et_2N \cdot CS$; d; R^1 = R^2 = Ac; e; R^1 = R^2 = H

(3): a; R = $OSO_2 \cdot C_6H_4Me$-p; b; R = $Pr^iO \cdot CO \cdot O$; c; R = $Et_2N \cdot CO \cdot O$; d; R = $\overline{N \cdot [CH_2]_4 \cdot CH_2} \cdot CS \cdot O$; e; R = $Et_2N \cdot CS \cdot O$; f; R = $Me_2N[CH_2]_2NMe \cdot CS \cdot O$; g; R = OH; h; R = H; i; R = $MeS \cdot CS \cdot O$

(4): a; R = $MeCS \cdot O$; b; R = $PhC(=NH) \cdot O$; c; R = H; d; R = OH; e; R = $EtO \cdot CO \cdot O$; f; R = $Pr^iO \cdot CO \cdot O$; g; R = $\overline{N \cdot [CH_2]_4 \cdot CH_2} \cdot CO \cdot O$

(5): a; R^1 = R^2 = $EtO \cdot CO \cdot O$; b; R^1 = R^2 = $Pr^iO \cdot CO \cdot O$; c; R^1 = R^2 = $MeS \cdot CS \cdot O$; d; R^1 = R^2 = $EtNH \cdot CS \cdot O$; e; R^1 = R^2 = $\overline{N \cdot [CH_2]_4 \cdot CH_2} \cdot CS \cdot O$; f; R^1 = R^2 = OH; g; R^1 = H, R^2 = OH; h; R^1 = R^2 = OAc; i; R^1 = $MeS \cdot CS \cdot O$, R^2 = $MeS \cdot CO \cdot O$; j; R^1 = R^2 = $ClCO \cdot O$; k; R^1 = R^2 = $Bu^tO \cdot CO \cdot O$; l; R^1 = R^2 = $\overline{N \cdot [CH_2]_4 \cdot CH_2} \cdot CO \cdot O$; m; R^1 = $MeS \cdot CS \cdot O$; R^2 = OH; n; R^1 = R^2 = $Bu^tNH \cdot CS \cdot O$; o; R^1 = $Bu^tNH \cdot CS \cdot O$, R = $MeS \cdot CS \cdot O$

(6): $Et_2N \cdot CS \cdot O \cdot C_{18}H_{37}$-n

(7): a; R = $Et_2N \cdot CS \cdot O$; b; R = OH; c; R = H

(8): C_8H_{17}-n

Dissolving-metal reduction of carbonate derivatives *etc.* at room temperature unless indicated to the contrary

Entry	Substrate (mmol)	Metal (mg-atom)	18-Crown-6 (mmol)	Solvents (ml)	Products
1 [a]	(1a), 3.75	K, 33	7.6	Bu^tNH_2, 25; Et_2O, 4	Decan-1-yl and decan-2-yl acetates, 5%; decane-1,2-diyl diacetate, 67%
2 [b]	(1b), 3.81	K, 49	13.25	Bu^tNH_2, 25; THF, 5	Dec-1-ene, 5%; decan-1-yl acetate, 26%; decan-2-yl acetate, 8%; decane-1,2-diyl diacetate, 35%
3 [a]	(2a), 1.77	K, 13	3.26	Bu^tNH_2, 20; THF, 5	Diacetate (2d), 69%
4	(2b), 0.40	K, 15	1.90	DME, 8; THF, 1	Intractable mixture
5	(2c), 1.40	K, 28	9.47	Bu^tNH_2, 20; THF, 5	Intractable mixture
6	(3a), 1.29	K, 15	2.27	Bu^tNH_2, 15; THF, 8	5α-Cholestan-3β-ol (3g), 73%
7	(3b), 1.02	K, 15	6.0	Bu^tNH_2, 25; THF, 4	5α-Cholestan-3β-ol (3g), 83%; 5α-cholestane (3h), 12%
8	(3c), 0.91	K, 23	5.3	Bu^tNH_2, 30; THF, 6	5α-Cholestan-3β-ol (3g), 80%; 5α-cholestane (3h), 4%
9	(3d), 0.71	K, 19	4.0	DME, 10; THF, 5	5α-Cholestan-3β-ol (3g), 14%; 5α-cholestane (3h), 74%
10	(3e), 0.64	K, 5.0	1.6	Bu^tNH_2, 8; THF, 6	5α-Cholestan-3β-ol (3g), 8%; 5α-cholestane (3h), 86%
11 [c]	(3e), 0.73	K, 20	5.7	Bu^tNH_2, 40; THF, 10	5α-Cholestan-3β-ol (3g), 40%; 5α-cholestane (3h), 58%
12	(3f), 0.58	K, 20	7.6	Bu^tNH_2, 20; THF, 4	5α-Cholestan-3β-ol (3g), 12%; 5α-cholestane (3h), 83%
13	(4a), 1.15	K, 15	8.71	Bu^tNH_2, 25; THF, 6	Cholest-5-ene (4c), 6%; cholesterol (4d), 87%
14	(4b), 0.34	Li, 43		$EtNH_2$, 4	Cholesterol (4d), 75%
15	(5a), 0.15	K, 13	3.4	Bu^tNH_2, 8; THF, 2	5α-Cholestane-3β,6β-diol (5f), 30%; 5α-Cholestan-3β-ol (3g), 20%
16	(5a), 0.11	Li, 14		$EtNH_2$, 3	5α-Cholestane-3β,6β-diol (5f), 66%
17	(5b), 0.17	K, 13	3.8	Bu^tNH_2, 5; THF, 1	5α-Cholestane-3β,6β-diol (5f), 24%; 5α-cholestan-3β-ol (3g), 41%
18 [a]	(5c), 0.06	Li, 11		$EtNH_2$, 2; THF, 0.5	5α-Cholestane-3β,6β-diyl diacetate (5h), 38%
19	(5c), 0.32	K, 26	9.46	Bu^tNH_2, 10; THF, 3	5α-Cholestane-3β,6β-diol (5f), 8%; 5α-Cholestan-3β-ol (3g), 19%; 5α-cholestan-6β-ol (5g), 2%; 5α-cholestane (3h), 38%
20	(5d), 0.06	Li, 14		$EtNH_2$, 2	5α-Cholestane-3β,6β-diol (5f), 68%
21	(5d), 0.21	K, 8.0	1.4	Bu^tNH_2, 8; THF, 2	5α-Cholestane-3β,6β-diol (5f), 45%; 5α-Cholestan-3β-ol (3g), 18%
22	(5e), 0.20	K, 11	1.6	Bu^tNH_2, 10; THF, 1	5α-Cholestane-3β,6β-diol (5f), 5%; 5α-Cholestan-3β-ol (3g), 12%; 5α-cholestan-6β-ol (5g), 15%; 5α-cholestane (3h), 62%
23	(6), 1.42	K, 23	4.2	Bu^tNH_2, 15; THF, 5	n-Octadecane, 87%; n-octadecan-1-ol, 12%
24	(7a), 2.45	K, 26	4.92	Bu^tNH_2, 20; THF, 4	(7b), 55%; (7c), 14%
25 [d]	(8), 4.42	K, 43	6.63	Bu^tNH_2, 10; Et_2O, 3	n-Decan-2-yl 3,5-dinitrobenzoate, 38%

[a] Crude reaction mixture acetylated (Ac_2O–pyridine) prior to separation. [b] Blue colour only restored after the addition of more potassium (26 mg-atom) and 18-crown-6 (6.43 mmol). Tabulated quantities are totals. The crude reaction mixture was acetylated (AcCl–pyridine) prior to separation. [c] Reaction carried out at −30 °C. [d] Extra crown ether (1.14 mmol) added after oxiran (8) to restore blue colour; tabulated volume is total. Crude decan-2-ol acylated [3,5-$(O_2N)_2C_6H_3COCl$–pyridine–benzene] to facilitate product isolation.

amate (7a) gave the 3-deoxyglucose derivative (7c) albeit in poor yield (14%).

n-Octyloxiran (8) reacted with potassium and 18-crown-6 to give a mixture of products from which decan-2-ol (38%) was isolated as its 3,5-dinitrobenzoate. The dissolving-metal reduction of epoxides has been described elsewhere.[4] The ring cleavage was considered to proceed *via* the oxiran dianion not the corresponding radical anion thereby producing the more substituted alcohol.

Clearly the reduction of *NN*-dialkylaminothiocarbonyloxyalkanes with potassium and 18-crown-6 provides a convenient method for the deoxygenation of alcohols.

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage and are uncorrected. Optical rotations were recorded on chloroform solutions. Preparative layer chromatography, p.l.c., was carried out on Merck Kieselgel GF_{254}, developing solvents

are given in parentheses. Column chromatography was carried out on Merck Kieselgel H or 60 or B.D.H. MFC grade materials using gradients of light petroleum–benzene–diethyl ether as eluants. Dec-1-ene (eluant petroleum), decan-1- and -2-yl acetates [eluant benzene–petroleum (1 : 4)] were separated from decane-1,2-diyl diacetate [eluant benzene–petroleum (1 : 1)] by chromatography on Kieselgel H; the ratio of the monoacetates was determined by g.l.c. (10% silicone OV-17 on Chromosorb, retention times: dec-1-ene 1.2 min, decan-1-yl acetate 9.6 min, decan-2-yl acetate 7.0 min). Solvents and reagents were purified by standard procedures.[5] Light petroleum and petroleum respectively refer to the redistilled reagents with b.p. 40—60 °C and 60—80 °C. 18-Crown-6 refers to the dry doubly distilled material purified *via* its acetonitrile complex;[6] commercial reagent is unsatisfactory unless purified. THF and 1,2-dimethoxyethane (DME) were freshly distilled from potassium–benzophenone; t-butylamine was freshly distilled from potassium. Nitrogen was purified by bubbling sequentially through aqueous chromium(II) chloride, concentrated sulphuric acid, phosphorus pentaoxide on glass wool, and sodium hydroxide pellets. Work-up refers to the dilution of the reaction mixture with water, extraction into diethyl ether, washing the organic phase with water, drying over anhydrous sodium or magnesium sulphate, filtration, and rotary-evaporation at ≤60 °C. The following compounds were prepared by standard procedures or authenticated by comparisons with literature data: (2a), m.p. 145—147 °C (lit.,[7] 146.5—147°); (2d), m.p. 122—123 °C, $[\alpha]_D^{23}$ +27.1° (*c* 1.359) (lit.,[8] 123 °C + 26.7°); (2e), m.p. 121—122 °C (lit.,[9] 122°), (3a), m.p. 136—137 °C (lit.,[10] 134—135 °C); (3g), (3h), (4c), (4d), (5f), (5g), (5h), octadecan-1-ol, and octadecane (see ref. 1 and references therein); (3i);[3,11] (4a);[3] (4b);[12] (7a), m.p. 51—53 °C, $[\alpha]_D^{23}$ −55.2° (*c* 1.045) [lit.,[13] 51—53°, −38° (dioxan)]; (7b), m.p. 110—111 °C (lit.,[14] 110—111 °C); (7c);[3] (8), b.p. 97—99 °C at 20 mmHg (lit.,[15] 89 °C at 10 mmHg); decan-1-yl acetate,[16] decan-2-yl acetate,[17] decane-1,2-diyl diacetate;[17] decane-1,2-diol, m.p. 47—49 °C (lit.,[15] 48—49 °C); and decan-2-yl 3,5-dinitrobenzoate, m.p. 41—42 °C (lit.,[17] 44 °C).

Reductions using Potassium, 18-Crown-6, and t-Butylamine, an Example.—Small clean oil-free pieces of potassium (600 mg) were added to a solution of 18-crown-6 (2.3 g) in dry t-butylamine (25 ml) under dry oxygen-free nitrogen. On stirring a royal-blue solution was rapidly obtained. Immediately a solution of the thioacetate (4a) (510 mg) in dry THF (6 ml) was added dropwise at such a rate that the blue colour was not discharged for long periods of time. When the addition was complete excess of ethanol was added to destroy the remaining potassium. After evaporation the residue was partitioned between diethyl ether and water. The organic phase was washed with water, dried, and evaporated, and the residue chromatographed on Kieselgel H (10 g) to give (eluant diethyl ether–petroleum gradient) cholest-5-ene (4c) (27 mg, 6%) and cholesterol (4d) (384 mg, 87%). Details of further reductions are summarised in the Table.

Reductions using Lithium and Ethylamine, an Example.—Ethylamine (4.0 ml) was distilled from sodium hydroxide pellets into a dry flask containing the benzimidate (4b) (166 mg) under dry oxygen-free nitrogen. Lithium (300 mg) was added and the mixture stirred until blue in colour. Methanol was added to quench the excess of metal and solvents were removed under reduced pressure. The residue was partitioned between diethyl ether and water. The organic phase was washed with hydrochloric acid (1M) and water, dried, and evaporated to give cholesterol (4d) (98 mg, 75%). Further reductions are tabulated. When a co-solvent is noted in the Table, the ester in co-solvent was added after the lithium, slowly, so as not to discharge the blue solution for long periods of time.

D,L-4-*Octyl*-1,3-*dioxolan*-2-*one* (1a).—To a solution of phosgene (2.0 g) in dichloromethane (50 ml) a solution of decane-1,2-diol (3.5 g) in dichloromethane (20 ml) and pyridine (10 ml) was added with stirring and cooling, and the mixture stirred at 20 °C for 16 h. Work-up and chromatography on Kieselgel 60 (45 g) gave on elution with diethyl ether–petroleum (1 : 9) a mixture of three unidentified minor products. Elution with diethyl ether–petroleum (2 : 3) gave the *cyclic carbonate* (1a) (2.9 g, 72%), $\nu_{max.}$ (film) 1 820—1 780, 1 160, 770, and 720 cm^{-1}, δ(CCl_4) 0.8—1.7 (17 H, m), 3.7—4.1 (1 H, m), and 4.2—4.7 (2 H, m); *m/e* 201 ($M^{+\cdot}$ + 1), 200 ($M^{+\cdot}$), 199 ($M^{+\cdot}$ − 1), 138, 110, 109, 96, 82, 67, and 55 (Found: C, 66.0; H, 10.3. $C_{11}H_{20}O_3$ requires C, 65.95; H, 10.05%).

D,L-4-*Octyl*-1,3-*dioxolan*-2-*thione* (1b).—To a solution of decane-1,2-diol (3.5 g) in THF (30 ml), a solution of *NN'*-thiocarbonyldi-imidazole (5.2 g) in THF (15 ml) was added and the mixture refluxed under nitrogen for 18 h. The solvent was removed under reduced pressure, the residue dissolved in dichloromethane, washed thoroughly with hydrochloric acid (1M) and brine, dried, and the solvent removed under reduced pressure. The crude product was chromatographed on Kieselgel 60 (32 g); elution with diethyl ether–petroleum (1 : 49) gave a minor non-u.v.-active product. Further elution with diethyl ether–petroleum (1 : 19) gave the *cyclic thiocarbonate* (1b) (2.8 g, 64%), $\nu_{max.}$ (film) 1 320—1 270, 1 165, and 980 cm^{-1}; δ($CDCl_3$) 0.8—2.00 (17 H, m), 4.1—4.5 (1 H, m), and 4.6—5.1 (2 H, m); *m/e* 216 ($M^{+\cdot}$), 183, 138, 109, 83, and 54 (Found: C, 61.15; H, 9.5. $C_{11}H_{20}O_2S$ requires C, 61.1; H, 9.3%).

1,2:5,6-*Di*-O-*Isopropylidene*-3,4-O-*thiocarbonyl*-D-*mannitol* (2b).—To a solution of 1,2:5,6-di-*O*-isopropylidene-D-mannitol (2e) (1.2 g) in THF (20 ml) *NN'*-thiocarbonyldi-imidazole (1.65 g) was added and the mixture refluxed for 7 h under nitrogen. The solvent was removed and the residue dissolved in dichloromethane, washed with cold dilute hydrochloric acid, and water, dried, and the solvent removed under reduced pressure. The residue was recrystallised from ethyl acetate–light petroleum to give the *product* (2b) (1.18 g, 85%) as white needles, m.p. 165—166.5 °C, $[\alpha]_D^{23}$ −15.6° (*c* 0.154), $\nu_{max.}$ (Nujol) 1 330, 1 300, 1 260, 1 245, 1 205, 1 165, 1 145, 1 060, 980, 960, 860, and 835 cm^{-1}; $\lambda_{max.}$ (EtOH) 234 (ε 15 000) and 267 nm (600); δ($CDCl_3$) 1.35 and 1.45 (12 H, 2s, Me_2C), 3.9—4.4 (6 H, m, 1-, 2-, 5-, 6-H), and 4.5—4.8 (2 H, m, 3-, 4-H); *m/e* 304 ($M^{+\cdot}$), 289 ($M^{+\cdot}$ −Me), and 101 (Found: C, 51.4; H, 6.65. $C_{13}H_{20}O_6S$ requires C, 51.3; H, 6.6%).

3β,6β-*Bis*(*chlorocarbonyloxy*)-5α-*cholestane* (5j).—To a solution of phosgene (4.9 g) in ethanol-free chloroform (30 ml) a solution of 5α-cholestane-3β,6β-diol (5f) (1.51 g) in chloroform (60 ml) and pyridine (700 mg) was added dropwise at 0 °C, and the mixture was allowed to stand at 23 °C for 17 h. When the optical rotation of the solution stabilized {$[\alpha]_D^{23}$ −30.4 (*c* 1.557)} the excess of phosgene was removed under reduced pressure to give the bis-chloroformate (5j) (1.98 g, 100%), δ($CDCl_3$) 0.72 (3 H, s, 13-Me), 1.03 (3 H, s, 10-Me), 4.66 (1 H, br, W_H 18 Hz, 3α-H), 4.93 (1 H, m, W_H

8 Hz, 6α-H). The product was used in the next step without further purification.

3β,6β-*Bis(ethoxycarbonyloxy)*-5α-*cholestane* (5a).—To solid 3β,6β-bis(chlorocarbonyloxy)-5α-cholestane (5j) (657 mg) absolute ethanol (20 ml) was added, followed by pyridine (2 ml); the mixture was then allowed to stand at 23 °C for 24 h. The solvents were removed under reduced pressure and the residue diluted with water and extracted with ether. The organic phase was dried, filtered, and separated by p.l.c. (benzene) to give 3β-ethoxycarbonyloxycholest-5-ene (4e) (179 mg, 31%) as needles from dichloromethane–methanol, m.p. 83·—84 °C (lit.,[18] m.p. 83—84 °C), δ($CDCl_3$), 0.67 (3 H, s, 13-Me), 1.00 (3 H, s, 10-Me), 1.23 (3 H, t, *J* 7 Hz, CH_3CH_2O), 4.17 (2 H, q, *J* 7 Hz, CH_3CH_2O), 4.7 (1 H, m, 3α-H), and 5.4 (1 H, m, W_H 8 Hz, 6-H); and the *dicathylate* (5a) (431 mg, 63%), which recrystallised from dichloromethane–methanol as prisms, m.p. 144—145 °C, $[\alpha]_D^{23}$ −21.1° (*c* 0.384), $\nu_{max.}$ ($CHCl_3$) 1 735 and 1 270—1 190 cm^{-1}; δ($CDCl_3$) 0.67 (3 H, s, 13-Me), 1.00 (3 H, s, 10-Me), 1.27 (6 H, t, *J* 7 Hz, $2CH_3CH_2O$), 4.10 (4 H, q, *J* 7 Hz, $2CH_3CH_2O$), 4.6 (1 H, m, 3α-H), and 4.8 (1 H, m, W_H 7 Hz, 6α-H); *m/e* M^+ absent, 458 ($M^{+\cdot}$ − EtOH − CO_2), 368, 353, 260, 255, 247, 228, 213, 147, and 81 (Found: C, 72.1; H, 10.3. $C_{33}H_{56}O_6$ requires C, 72.2; H, 10.3%).

3β,6β-*Bis(isopropoxycarbonyloxy)*-5α-*cholestane* (5b).—To solid 3β,6β-bis(chlorocarbonyloxy)-5α-cholestane (5j) (657 mg), absolute propan-2-ol (20 ml) was added followed by pyridine (2 ml) and the mixture was allowed to stand for 24 h at 23 °C. Work-up and p.l.c. (benzene) gave 3β-(*isopropyloxycarbonyloxy*)*cholest-5-ene* (4f) (146 mg, 25%), which was crystallised from acetone, m.p. 110—111 °C, $[\alpha]_D^{23}$ −32.1° (*c* 1.636), $\nu_{max.}$ (CCl_4) 1 735 and 1 260 cm^{-1}; δ($CDCl_3$) 0.67 (3 H, s, 13-Me), 1.00 (3 H, s, 10-Me), 1.30 (6 H, d, *J* 6 Hz, Me_2CHO), 4.4 (1 H, m, W_H 17 Hz, 3α-H), 4.9 (1 H, m, Me_2CHOCO), and 5.4 (1 H, m, W_H 8 Hz, 6-H); *m/e* 472 ($M^{+\cdot}$), 368, 353, 260, 247, 227, 147, and 81 (Found: C, 78.95; H, 11.3. $C_{31}H_{52}O_3$ requires C, 78.75; H, 11.1%); and 3β,6β-*bis(isopropyloxycarbonyloxy)*-5α-*cholestane* (5b) (517 mg, 72%), recrystallised from chloroform–methanol, m.p. 122—124 °C, $[\alpha]_D^{23}$ −21.3° (*c* 0.954), $\nu_{max.}$ ($CHCl_3$) 1 730 and 1 270—1 190 cm^{-1}; δ($CDCl_3$) 0.68 (3 H, s, 13-Me), 1.01 (3 H, s, 10-Me), 1.30 (12 H, d, *J* 6 Hz, Me_2CHOCO), and 4.27—5.33 (4 H, m, 3α-H, 6α-H, $2CHMe_2$), *m/e* $M^{+\cdot}$ absent, 472, 368, 318, 255, 247, 228, 213, and 81 (Found: C, 72.9; H, 10.6. $C_{35}H_{60}O_6$ requires C, 72.85; H, 10.5%).

Attempted Preparation of 3β,6β*Bis-(t-butoxycarbonyloxy)*-5α-*cholestane* (5k).—To a solution of the dichloroformate (5j) (197 mg) in t-butyl alcohol (10 ml) resublimed potassium t-butoxide (188.8 mg) was added and the mixture allowed to stand at 60 °C for 2 days. The solvent was removed under reduced pressure, the residue diluted with water, extracted with ether, and the organic phase dried and evaporated to give cholesterol (4d) (130 mg, 90%).

3β-(*Isopropyloxycarbonyloxy*)-5α-*cholestane* (3b).—To a solution of phosgene (6.4 g) in dichloromethane (30 ml) a solution of 5α-cholestan-3β-ol (3g) (3.0 g) in dichloromethane (50 ml) and pyridine (2 ml) was added at 0 °C over a 0.25 h period; the mixture was then allowed to stand for 17 h at 20 °C. The excess of phosgene and solvent were removed under reduced pressure, and the residue was dissolved in propan-2-ol (32 ml) and pyridine (2 ml) and allowed to stand for 17 h at 20 °C. The solvent was removed under reduced pressure, and the residue worked up in the usual way, to give the 3β-carbonate (3b) (3.2 g, 87%) as leaflets from acetone, m.p. 84.5—85 °C, $[\alpha]_D^{23}$ +14.5° (*c* 1.660), $\nu_{max.}$ (Nujol) 1 740, 1 265, and 1 255 cm^{-1}; δ($CDCl_3$) 0.67 (3 H, s, 13-Me), 1.33 (6 H, d, *J* 7 Hz, Me_2CH), 4.5 (1 H, m, 3α-H), and 4.8 (1 H, m, Me_2CH); *m/e* 474 ($M^{+\cdot}$), 370, 355, 320, 230, 215, and 81 (Found: C, 78.65; H, 11.75. $C_{31}H_{54}O_3$ requires C, 78.45; H, 11.45%).

Attempted Preparation of 3β,6β-*Bis(piperidinocarbonyloxy)*-5α-*cholestane* (5l).—To solid dichloroformate (5j) (657 mg), piperidine (20 ml) was added and the mixture allowed to stand at 23 °C for 24 h. Work-up and p.l.c. [ethyl acetate–petroleum (3 : 7)] gave 3β-*piperidinocarbonyloxycholest-5-ene* (4g) (462 mg, 75%) as needles from chloroform–methanol, m.p. 178—181 °C, $[\alpha]_D^{23}$ −43.2° (*c* 0.247), $\nu_{max.}$ (Nujol) 1 705 cm^{-1}; δ($CDCl_3$) 0.67 (3 H, s, 13-Me), 1.00 (3 H, s, 10-Me), 3.36 (4 H, m, CH_2NCH_2), 4.43 (1 H, br, W_H 16 Hz, 3α-H), and 5.36 (1 H, m, W_H 8 Hz, 6-H); *m/e* 497 ($M^{+\cdot}$), 451, 368, 353, 260, 255, 247, 213, 147, and 81 (Found: C, 79.5; H, 11.2; N, 2.8. $C_{35}H_{55}NO_2$ requires C, 79.6; H, 11.15; N, 2.8%); and a minor uncharacterised product (50 mg) as needles from chloroform–methanol, m.p. 205—208 °C, $[\alpha]_D^{23}$ −21.3° (*c* 1.294), $\nu_{max.}$ ($CHCl_3$) 1 670, 1 260—1 190, 1 150, and 1 080—1 020 cm^{-1}; δ($CDCl_3$) 0.67 (3 H, s, 13-Me), 1.02 (3 H, s, 10-Me), 3.4 (5 H, m, CH_2NCH_2), 4.5 (1 H, m, 3α-H), and 4.6 (1 H, m, W_H 10 Hz, 6α-H); *m/e* 603, 577, 551, 386, 368, 353, 301, 275, 255, 247, 231, 213, 107, and 81 (Found: C, 78.4; H, 11.15; N, 3.3%).

3β-(NN-*Diethylaminocarbonyloxy*)-5α-*cholestane* (3c).—To a solution of phosgene (3.0 g) in dichloromethane (50 ml) triethylamine (10 ml) was added at 0 °C and the mixture allowed to stand for 5 h at 20 °C. A solution of 5α-cholestan-3β-ol (3g) (2.0 g) in dichloromethane (15 ml) was added and the mixture was stirred at 20 °C for 17 h. The solvents were removed under reduced pressure, the residue diluted with water and extracted with ether, and the organic phase was washed with water, dried, and evaporated. The residue was crystallised from ethanol and recrystallised from acetone to give the 3β-*carbamate* (3c) (2.0 g, 80%) as needles, m.p. 122—122.5 °C, $[\alpha]_D^{23}$ +17.2° (*c* 1.230), $\nu_{max.}$ (Nujol) 1 700, 1 270, and 1 170 cm^{-1}; δ(CCl_4) 0.67 (3 H, s, 10-Me), 1.23 (6 H, t, *J* 7 Hz, $2CH_3CH_2N$), 3.27 (4 H, q, *J* 7 Hz, $2CH_3CH_2N$), and 4.6 (1 H, m, W_H 18 Hz, 3α-H); *m/e* 487 ($M^{+\cdot}$), 486, 472, 428, 370, 355, 316, 257, 215, 118, 95, and 81 (Found: C, 79.05; H, 12.05; N, 2.9. $C_{32}H_{57}NO_2$ requires C, 78.8; H, 11.8; N, 2.85%).

3β,6β-*Bis*[(*methylthio*)*thiocarbonyloxy*]-5α-*cholestane* (5c).—To a solution of 5α-cholestane-3β,6β-diol (5f) (400 mg) in THF (10 ml), sodium hydride (80%, 150 mg) was added and the mixture refluxed for 24 h under nitrogen. Carbon disulphide (0.15 ml) was added at 23 °C followed after 1 h by iodomethane (0.20 ml). The mixture was stirred at 23 °C for further 1 h, and the excess of sodium hydride quenched by acetic acid (0.5 ml), followed by water (1 ml). The mixture was extracted with diethyl ether and the organic phase washed with sodium hydrogencarbonate, dried, and separated by p.l.c. [diethyl ether–petroleum (1 : 19)] to give 3β-[(*methylthio*)*thiocarbonyloxy*]-6β-[(*methylthio*)*carbonyloxy*]-5α-*cholestane* (5i) (300 mg, 51%), m.p. 162—163.5 °C (from dichloromethane–methanol), $[\alpha]_D^{23}$ −54.1° (*c* 0.562), $\nu_{max.}$ (Nujol) 1 700, 1 225, 1 135, and 1 060 cm^{-1}; $\nu_{max.}$ (cyclohexane) 1 720, 1 220, 1 135, 1 060—1 010, and 760 cm^{-1}; $\lambda_{max.}$ (cyclohexane) 276 (ε 11 000), 225 (8 000), and 207 nm (9 000); δ($CDCl_3$) 0.67 (3 H, s, 13-Me), 1.03 (3 H, s, 10-Me), 2.28 (3 H, s, MeS·CO·O), 2.52 (3 H, s,

MeS·CS·O), and 5.05 (1 H, m, W_H 8 Hz, 6β-H), and 5.5 (1 H, br, W_H 16 Hz, 3α-H); *m/e* 568 ($M^{+\cdot}$), 518, 507, 460, 402, 368, 255, 161, 95, and 81 (Found: C, 65.6; H, 8.9. $C_{31}H_{52}O_3S_3$ requires C, 65.45; H, 9.2%); and 3β-[(methylthio)thiocarbonyloxy]-5α-cholestan-6β-ol (5m) (120 mg), δ($CDCl_3$) 0.68 (3 H, s, 13-Me), 1.00 (3 H, s, 10-Me), 2.33 (3 H, s, CH_3S·CS·O), 3.56 (1 H, m, 6α-H), and 5.0 (1 H, br, 3α-H). The latter was taken up in THF (5 ml) and a solution of n-butyl-lithium (1.6M; 1 ml) in hexane was added at −20 °C followed after 3 h by carbon disulphide (1 ml) and iodomethane (3 ml) after a further 2 h. The reection was quenched with acetic acid (1 ml), worked up, and chromatographed [p.l.c.; diethyl ether–petroleum (1 : 19)] to give 3β,6β-*bis*[(*methylthio*)*thiocarbonyloxy*]-5α-*cholestane* (5c) (45 mg, 8%) which was recrystallised from diethyl ether–methanol, m.p. 136—138 °C, $[\alpha]_D^{23}$ −53.9° (*c* 0.193), $\nu_{max.}$ ($CHCl_3$) 1 170, 1 150, 1 060—1 030, and 965 cm^{-1}; $\lambda_{max.}$ (cyclohexane) 276 (ε 20 000), 227 (15 000), and 210 nm (15 000); δ($CDCl_3$) 0.67 (3 H, s, 13-Me), 1.08 (3 H, s, 10-Me), 2.53 and 2.55 (6 H, 2s, 2*Me*S·CS·O), 5.4 (1 H, m, W_H 20 Hz, 3α-H), and 5.73 (1 H, m, W_H 7 Hz, 6α-H); *m/e* $M^{+\cdot}$ (absent), 476 ($M^{+\cdot}$ − MeSH-COS), 368, 353, 255, 95, and 81 (Found: C, 63.85; H, 8.7. $C_{31}H_{52}O_2S_4$ requires C, 63.7; H, 8.95%). To a solution of the 3β,6β-diol (5f) (400 mg) in THF (10 ml) n-butyl-lithium (1.6M; 3.12 ml) was added at −20° with stirring under nitrogen. The mixture was stirred for 2.5 h when carbon disulphide (0.5 ml) was added. Stirring was continued for 1 h after which iodomethane (0.5 ml) was added. After the mixture had been stirred for a further 1 h, acetic acid (1 ml) was added followed by water (1 ml); the mixture was then extracted with ether. The ether layer was washed with water and dried, and the residue chromatographed on neutral grade I alumina (8 g) (eluant petroleum). The residue on evaporation was crystallised from chloroform–methanol to give the product (5c) as needles (310 mg, 53%).

3β,6β-*Bis*(*ethylaminothiocarbonyloxy*)-5α-*cholestane* (5d).—To a solution of 5α-cholestane-3β,6β-diol (5f) (404 mg) in THF (10 ml) a solution of n-butyl-lithium (1.54M; 3 ml) was added at 23 °C under nitrogen and with stirring. After 1 h carbon disulphide (2 ml) was added followed after 1 h by iodomethane (2 ml). The reaction mixture was quenched with acetic acid (1 ml) and worked up. The crude product was treated with ethylamine (20 ml), the amine removed after 1 h, and the product separated by p.l.c. [diethyl ether–petroleum (2 : 3)] to give the *bisthiocarbamate* (5d) (450 mg, 78%), m.p. 169—172 °C, plates from methanol, $[\alpha]_D^{23}$ −31.3° (*c* 0.495), $\nu_{max.}$ ($CHCl_3$) 3 430, 3 400, 3 240, 1 330, 1 295, 1 120, 1 050, 1 000, 960, and 910 cm^{-1}; $\lambda_{max.}$ (EtOH) 242.5 nm (ε 26 000); δ($CDCl_3$) 0.67 (3 H, s, 13-Me), 3.5 (4 H, m, 2CH_3CH_2N), 5.3 (1 H, m, W_H 18 Hz, 3α-H), 5.6 (1 H, m, W_H 8 Hz, 6α-H), 6.2 and 7.2 (2 H, 2m, exch. D_2O, 2N*H*); *m/e* 578 ($M^{+\cdot}$), 473, 402, 386, 368, 353, 255, 247, 213, 81, and 60 (Found: C, 68.7; H, 10.3; N, 4.8. $C_{33}H_{58}N_2O_2S_2$ requires C, 68.45; H, 10.1; N, 4.85%).

Attempted Preparation of 3β,6β-*Bis*-(*t-butylaminothiocarbonyloxy*)-5α-*cholestane* (5n).—The dixanthate (5c) (300 mg) was dissolved in Bu^tNH_2 (15 ml) and the solution allowed to stand at 23 °C for 7 days; it was then refluxed for 4 days. Work-up and p.l.c. [diethyl ether–petroleum (2 : 23)] gave an oil probably 3β-(t-butylaminothiocarbonyloxy)-6β-[(methylthio)thiocarbonyloxy]-5α-cholestane (5o), δ($CDCl_3$) 0.67 (3 H, s, 13-Me), 1.08 (3 H, s, 10-Me), 1.32 (9 H, s, Bu^t), 2.55 (3 H, s, MeS), 5.3 (1 H, m, W_H 16 Hz, 3α-H), 5.8 (1 H, m, W_H 7 Hz, 6α-H), and 6.7 (1 H, br, N*H*), which was redissolved in Bu^tNH_2 and heated in a sealed vessel to give a mixture of compounds.

3β,6β-*Bis*(*pyrrolidin-1-ylthiocarbonyloxy*)-5α-*cholestane* (5e).—The dixanthate (5c) (300 mg) was allowed to stand in pyrrolidine (5 ml) at 23 °C for 18 h after which the solvent was removed and the crude product chromatographed on MFC silica [eluant diethyl ether–petroleum (1 : 4)] and crystallised from acetone to give the *bisthiocarbamate* (5e) as white rods (230 mg, 71%), m.p. 236—238 °C, $[\alpha]_D^{23}$ −23.3° (*c* 0.952), $\nu_{max.}$ (Nujol) 1 260 and 1 230 cm^{-1}; $\lambda_{max.}$ (EtOH) 245 nm (ε 27 000), δ($CDCl_3$) 0.67 (3 H, s, 13-Me), 1.05 (3 H, s, 10-Me), 3.3—4.0 (8 H, m, 2CH_2NCH_2), 5.27 (1 H, m, W_H 22 Hz, 3α-H), and 5.6 (1 H, m, W_H 7 Hz, 6α-H); *m/e* 630 (M^+ at 12 eV), 499, 466, 368, 353, 255, 247, 213, 132, and 81 (Found: C, 70.5; H, 9.95; N, 4.45. $C_{37}H_{62}N_2O_2S_2$ requires C, 70.4; H, 9.9; N, 4.45%).

3β-(*Piperidinothiocarbonyloxy*)-5α-*cholestane* (3d).—To a suspension of sodium hydride (80%; 150 mg) and imidazole (10 mg) in THF (3 ml) a solution of 5α-cholestan-3β-ol (3g) (1.17 g) was added and the mixture refluxed for 3 h under nitrogen. Carbon disulphide (1 ml) was added at 23 °C followed by iodomethane (1 ml) and piperidine (4 ml) and the mixture stirred for 16 h at 23 °C. Further piperidine (4 ml) was added and the mixture refluxed for 2 h; the solvents were then removed under reduced pressure, and the residue crystallised from ether–methanol and recrystallised from light petroleum to give the *thiocarbamate* (3d) (1.08 g, 70%), m.p. 190.5—191.5°, $[\alpha]_D^{23}$ +10.0° (*c* 0.52); $\nu_{max.}$ (Nujol) 1 500, 1 460, 1 430, 1 290, 1 260, 1 250 and 1 180 cm^{-1}; δ($CDCl_3$) 0.63 (3 H, s, 13-Me), 0.91 (3 H, s, 10-Me), 3.43—4.26 (4 H, m, CH_2NCH_2), and 5.28 (1 H, m, W_H 24 Hz, 3α-H) (Found: C, 76.85; H, 11.1; N, 2.7. $C_{33}H_{57}NOS$ requires C, 76.85; H, 11.15; N, 2.7%).

3β-(NN-*Diethylaminothiocarbonyloxy*)-5α-*cholestane* (3e).—To a solution of the xanthate (3i) (620 mg) in light petroleum (10 ml) diethylamine (10 ml) was added and the solution allowed to stand at 23 °C for 66 h. The solvents were removed under reduced pressure and the residue chromatographed on neutral grade I alumina (20 g) [eluant diethyl ether–light petroleum (3 : 97)] and the product recrystallised from acetone to give the *thiocarbamate* (3e) (600 mg, 92%), m.p. 137—139 °C, $[\alpha]_D^{23}$ +7.9° (*c* 1.191), $\nu_{max.}$ (Nujol) 1 510, 1 315, 1 285, 1 250, 1 240, and 1 180 cm^{-1}, $\lambda_{max.}$ (EtOH) 248.5 nm (ε 12 500); δ(CCl_4) 0.67 (3 H, s, 13-Me), 1.20 (6 H, 2t, 2CH_3CH_2N), 3.16—4.06 (4 H, m, 2CH_3CH_2N), and 5.27 (1 H, m, W_H 18 Hz, 3α-H); *m/e* 503 ($M^{+\cdot}$), 370, 355, 316, 215, 135, 100, 95, and 81 (Found: C, 76.45; H, 11.6; N, 2.75. $C_{32}H_{57}NOS$ requires C, 76.3; H, 11.4; N, 2.8%).

N-*Methyl*-N-[2-(NN-*dimethylamino*)*ethyl*]*aminothiocarbonyloxy*-5α-*cholestane* (3f).—To a solution of the xanthate (3i) (520 mg) in petroleum (9 ml), *NNN'*-trimethylethylenediamine (3 ml) was added and the mixture allowed to stand at 23 °C for 3 days. The solvents were removed under reduced pressure and the residue chromatographed on Merck alumina H (14 g) to give the *thiocarbamate* (3f) (485 mg, 84%) which solidified on standing, m.p. 91—92 °C, $[\alpha]_D^{23}$ +8.1° (*c* 1.186), $\nu_{max.}$ ($CHCl_3$) 2 780, 1 495, 1 400, 1 310, 1 290, 1 150, 1 130, 1 095, 1 010, 955, and 915 cm^{-1}; $\lambda_{max.}$ (EtOH) 247.5 nm (ε 15 000); δ(CCl_4) 0.63 (3 H, s, 13-Me), 2.23 (6 H, s, Me_2N), 2.50 (2 H, br t, *J* 8 Hz, CH_2NMe_2), 3.05 and 3.27 (3 H, 2s, *Me*NCH_2), 3.50 and 3.80 (2 H, 2t, *J* 7 Hz, MeNCH_2), and 5.17 (1 H, m, W_H 17 Hz, 3α-H); *m/e* 532 ($M^{+\cdot}$), 370, 355, 316, 85, 71, 58, 57, 55, and

43 (Found: C, 74.55; H, 11.55; N, 5.2. $C_{33}H_{60}N_2OS$ requires C, 74.4; H, 11.35; N, 5.25%).

1-(NN-*Diethylaminothiocarbonyloxy*)*octadecane* (6).—To a suspension of sodium hydride (50%, 2 g) and imidazole (50 mg) in THF (20 ml) a solution of octadecan-1-ol (5.0 g) in THF (30 ml) was added and the mixture was refluxed for 2 h under nitrogen. Carbon disulphide (6 ml) was added with stirring at 23 °C; after 0.5 h iodomethane (6 ml) was added. After the excess of sodium hydride had been quenched with acetic acid, diethylamine (50 ml) was added and the mixture stirred for 18 h at 23 °C. The solvents were removed under reduced pressure and the residue worked up and chromatographed on Kieselgel 60 (60 g) [eluant benzene–petroleum (1 : 4)] to give the *thiocarbamate* (6) (5 g, 70%) as fine needles, m.p. 37.5—38 °C from acetone–methanol, $\nu_{max.}$ (CCl_4) 1 495, 1 320, 1 280, 1 240, 1 180, 1 150, 1 095, 1 075, 1 040, and 990 cm^{-1}; $\lambda_{max.}$ (EtOH) 247.5 nm (ε 14 500); δ(CCl_4) 1.00 (6 H, t, *J* 7 Hz, $2CH_3CH_2$-N), 3.17—4.00 (4 H, m, $2CH_3CH_2N$), and 4.3 (2 H, t, *J* 7 Hz, CH_2CH_2O); *m/e* 385 ($M^{+\cdot}$), 384, 368, 352, and 134 (Found: C, 71.8; H, 12.55; N, 3.65. $C_{23}H_{47}NOS$ requires C, 71.6; H, 12.3; N, 3.65%).

2,4-*Bis*-O-(NN-*diethylaminothiocarbonyl*)-1,2:5,6-*di*-O-*isopropylidene*-D-*mannitol* (2c).—To a suspension of sodium hydride (80%, 3.0 g) and imidazole (50 mg) in THF (80 ml) a solution of 1,2:5,6-di-*O*-isopropylidene-D-mannitol (2e) (6.6 g) in THF (30 ml) was added and the mixture refluxed for 5.5 h. Carbon disulphide (6.0 g) was added at 20 °C and the mixture stirred for 0.5 h after which iodomethane (10 g) was added. The mixture was worked up after being stirred for 0.5 h. The crude product was dissolved in diethylamine (60 ml) and the solution was allowed to stand at 20 °C for 2 days. Work-up and chromatography on Kieselgel 60 (70 g) [eluant diethyl ether–petroleum (3 : 7)] gave the *bisthiocarbamate* (2c) (6.27 g, 51%) as needles from acetone, m.p. 104—105 °C, $[\alpha]_D^{23}$ +69.3° (*c* 1.298), $\nu_{max.}$ ($CHCl_3$) 1 500, 1 310, 1 280, 1 260—1 190, 1 155, 1 140, 1 060, 980, and 860 cm^{-1}; $\lambda_{max.}$ (EtOH) 248.5 nm (ε 29 500); δ 1.28, 1.3 (12 H, 2t, *J* 7 Hz, $4NCH_2CH_3$), 1.4, 1.43 (12 H, 2s, $2Me_2C$), 3.6, 3.9 (8 H, 2q, *J* 7 Hz, $4NCH_2CH_3$), 4.08 (4 H, m, 1-H, 1′-H, 6-H, 6′-H), 4.55 (2 H, m, 2-H, 5-H), and 6.4 (2 H, m, 3-H, 4-H); *m/e* 492 ($M^{+\cdot}$), 477, 359, 318, 258, 227, 217, 169, and 100 (Found: C, 53.85; H, 8.3; N, 5.7. $C_{22}H_{40}N_2O_6S_2$ requires C, 53.65; H, 8.2; N, 5.7%).

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