(0.4 mL) and the ketene alkyl silyl acetal (4 mL) in an atmosphere of N_2 were heated at 110 °C. After 0.5 h the excess of the ketene alkyl silyl acetal was distilled in vacuo; the residue was analyzed by GC (the percentages are shown in Table I) and then chromatographed on silica gel (hexane/ethyl acetate, 8:2), giving the products **2**,[14-16] **3**, and **4** in the yields reported in Table I.

3a: bp 80 °C (10 mmHg); IR 1730, 1710 cm^{-1}; ^1H NMR δ 4.37 (q, 1 H, CH), 4.15 (q, 2 H, CH_2O), 4.13 (q, 2 H, CH_2O), 1.42 (d, 3 H, CH_3CH), 1.29 (t, 3 H, CH_3CH_2O), 1.27 (t, 3 H, CH_3CH_2O), 0.11 (s, 9 H, $(CH_3)_3Si$); ^{13}C NMR δ 166.85 (CO), 160.51 (CN), 68.12 (CH), 62.97 (CH_2O), 61.74 (CH_2O), 22.17 (CH_3C), 14.19 (CH_3CH_2O), 13.81 (CH_3CH_2O), -0.53 ($(CH_3)_3Si$); mass spectrum, *m/z* (relative intensity) 261 (M^+, 23), 246 (7), 216 (23), 188 (34), 144 (46), 117 (100), 103 (19), 100 (23), 75 (15), 73 (61); HRMS, M^+, 261.1395, calcd for $C_{11}H_{23}NO_4Si$, 261.1396.

3b: bp 83 °C (10 mmHg); IR 1730, 1700 cm^{-1}; ^1H NMR δ 4.30-4.00 (m, 5 H, CH + 2 CH_2O), 1.86-1.66 (m, 2 H, CCH_2CH_3), 1.29 (t, 3 H, CH_3CH_2O), 1.27 (t, 3 H, CH_3CH_2O), 0.92 (t, 3 H, CH_3CH_2C), 0.11 (s, 9 H, $(CH_3)_3Si$); ^{13}C NMR δ 166.46 (CO), 160.46 (CN), 73.15 (CH), 62.89 (CH_2O), 61.73 (CH_2O), 28.83 (CCH_2CH_3), 14.21 (CH_3CH_2O), 13.87 (CH_3CH_2O), 9.76 (CH_3CH_2C), -0.57 ($(CH_3)_3Si$); mass spectrum, *m/z* (relative intensity) 275 (M^+, 26), 260 (11), 230 (23), 188 (43), 161 (10), 158 (37), 157 (15), 132 (15), 131 (100), 116 (15), 100 (24), 73 (37); HRMS, M^+, 275.1554, calcd for $C_{12}H_{25}NO_4Si$, 275.1552.

3c: bp 73 °C (10 mmHg); IR 1730 (br) cm^{-1}; ^1H NMR δ 4.16 (q, 2 H, CH_2O), 3.70 (s, 3 H, CH_3O), 1.50 (s, 6 H, $(CH_3)_2C$), 1.30 (t, 3 H, CH_3CH_2), 0.12 (s, 9 H, $(CH_3)_3Si$); ^{13}C NMR δ 166.96 (CO), 160.01 (CN), 76.35 ($C(CH_3)_2$), 61.61 (CH_2O), 54.46 (CH_3O), 28.49 ($(CH_3)_2C$, 14.13 (CH_3CH_2O), 2.12 ($(CH_3)_3Si$); mass spectrum, *m/z* (relative intensity) 246 (M^+ - 15, 16), 216 (16), 188 (23), 131 (94), 101 (20), 89 (13), 73 (100); HRMS, M^+ - 15, 246.1159, calcd for $C_{10}H_{20}NO_4Si$, 246.1161.

4a:[17] IR 3410, 1800, 1730 cm^{-1}; ^1H NMR δ 8.57 (br s, 1 H, NH), 4.28 (q, 2 H, CH_2O), 3.90 (q, 1 H, CH), 3.57 (q, 2 H, CH_2O), 1.46-1.10 (m, 8 H); ^{13}C NMR δ 171.52 (CCON), 150.33 (NCOO), 76.09 (CH), 65.42 (CH_2OCH), 62.00 (CH_2OCO), 17.73 (CH_3CH), 14.94 (CH_3CH_2OCH), 13.89 (CH_3CH_2OCO); mass spectrum, *m/z* (relative intensity) 189 (M^+, 2), 145 (11), 73 (100), 45 (67).

4b: bp 110 °C (3 mmHg); IR 3410, 1805, 1735 cm^{-1}; ^1H NMR δ 8.50 (s, 1 H, NH), 4.08 (q, 2 H, CH_2OCO), 3.61 (t, 1 H, CH), 3.41 (q, 2 H, CH_2O), 1.59 (m, 2 H, CH_2CH), 1.15 (t, 3 H, CH_3CH_2O), 1.09 (t, 3 H, CH_3CH_2O), 0.78 (t, 3 H, CH_3CH_2C); ^{13}C NMR δ 171.08 (CCON), 150.07 (NCOO), 80.84 (CH), 65.84 (CH_2OCH), 61.65 (CH_2OCO), 24.98 (CH_3CH_2C), 14.69 (CH_3CH_2OCH), 13.67 (CH_3CH_2OCO), 8.50 (CH_3CH_2C); mass spectrum, *m/z* (relative intensity) 203 (M^+, 1), 87 (65), 85 (66), 83 (100), 58 (49), 45 (24); HRMS, M^+ 203.1146, calcd for $C_9H_{17}NO_4$, 203.1157.

4c:[16] IR 3410, 1800, 1730 cm^{-1}; ^1H NMR δ 8.60 (br s, 1 H, NH), 4.25 (q, 2 H, CH_2OCO), 3.25 (s, 3 H, CH_3O), 1.40 (s, 6 H, $(CH_3)_2C$), 1.30 (t, 3 H, CH_3CH_2); ^{13}C NMR δ 173.39 (CCON), 150.83 (NCOO), 79.04 ($C(CH_3)_2$), 62.14 (CH_2OCO), 51.01 (CH_3O), 22.61 ($(CH_3)_2C$), 14.20 (CH_3CH_2); mass spectrum (50 eV), *m/z* (relative intensity) 189 (M^+, 2), 130 (8), 86 (9), 84 (15), 74 (32), 73 (100), 43 (55), 41 (33).

Reaction of Ethyl Azidoformate with Ketene Alkyl Silyl Acetals at Room Temperature. General Procedure. Ethyl azidoformate (0.2 mL) and the ketene silyl acetal (2 mL) in an atmosphere of N_2 were allowed to react at room temperature. When the azide band disappeared in the IR spectrum, the excess of the ketene silyl acetal was distilled in vacuo at room temperature. The residue was immediately analyzed by ^1H NMR. Spectra changed on standing and after 24 h the spectra of the mixtures were very similar to those of the reactions at 110 °C. The probable triazoline **6b** coming from **1b** was detected by ^1H NMR spectrum at 300 MHz: δ 4.35 (m, 2 H, CH_2OC), 3.91 (dd, 1 H, CH), 3.60-3.38 (m, 2 H, CH_2OC), 1.85-1.56 (m, 2 H, CH_2CH), 1.36 (t, 3 H, CH_3CH_2O), 1.21 (t, 3 H, CH_3CH_2O), 1.12 (t, 3 H, CH_3CH_2C). The percentages of the final mixtures are reported in Table I.

Photolysis of Ethyl Azidoformate with Ketene Alkyl Silyl Acetals. Ethyl azidoformate (0.2 mL) and the ketene silyl acetal (2 mL), in an atmosphere of N_2, were photolyzed in a quartz vessel using a medium pressure Hanovia PCR lamp (100 W). When the azide band disappeared in the IR spectrum the excess of the ketene silyl acetal was distilled in vacuo at room temperature. The residue was worked up as above, giving the products **2**, **3**, and **4** in the yields reported in Table I.

Hydrolysis of 3. **3b** (150 mg) was stirred with 5.4 mL of THF, 2.16 mL of acetic acid, and 0.54 mL of water at room temperature for 16 h. The mixture was neutralized by aqueous sodium bicarbonate solution and extracted with ethyl ether. The organic layer was washed with water and brine, dried on molecular sieves (4 Å), and then evaporated giving **5b**[18] (105 mg; 95%): IR 1750 cm^{-1}; ^1H NMR δ 4.85 (dd, 1 H, CH), 4.22 (2 q, 4 H, 2 CH_2O), 1.99-1.81 (m, 2 H, CH_2CH), 1.35-1.21 (m, 6 H, 2 CH_3CH_2O), 1.01 (t, 3 H, CH_3CH_2C); ^{13}C NMR δ 169.91 (CCO), 154.70 (OCO), 72.26 (CH), 64.41 (CH_2O), 61.33 (CH_2O), 24.55 (CH_2CH), 14.14 (CH_3CH_2O), 14.10 (CH_3CH_2O), 9.35 (CH_3CH_2C); mass spectrum, *m/z* (relative intensity) 205 (M^+ + 1, 27), 204 (M^+, 9), 176 (29), 159 (86), 131 (21), 130 (86), 115 (21), 114 (37), 102 (17), 87 (33), 73 (10), 59 (100).

The above procedure was followed for **3a**, giving **5a**[19] (70%): IR 1750 cm^{-1}; ^1H NMR δ 5.00 (q, 1 H, CH), 4.22 (q, 4 H, 2 CH_2O), 1.52 (d, 3 H, CH_3CH), 1.33 (t, 3 H, CH_3CH_2O), 1.29 (t, 3 H, CH_3CH_2O); ^{13}C NMR δ 170.43 (CCO), 154.38 (OCO), 71.48 (CH), 64.35 (CH_2O), 61.40 (CH_2O), 16.90 (CH_3CH), 14.12 (2 CH_3CH_2O); mass spectrum, *m/z* (relative intensity) 191 (M^+ + 1, 7), 190 (M^+, 12), 145 (65), 118 (47), 117 (58), 102 (31), 101 (22), 75 (10), 74 (11), 73 (33), 45 (100), 43 (16), 29 (67).

The hydrolysis of **3c** required more drastic conditions: 150 mg of **3c** was stirred with 6.0 mL of THF, 6.0 mL of acetic acid, and 1.5 mL of water at room temperature for 120 h, giving **5c**[19] (70%). A specimen of **5c** was prepared according to the reported procedure[18] starting from 2-hydroxybutanoic acid: IR 1750 cm^{-1}; ^1H NMR δ 4.18 (q, 2 H, CH_2O), 3.76 (s, 3 H, CH_3O), 1.61 (s, 6 H, $(CH_3)_2C$), 1.31 (t, 3 H, CH_3CH_2); ^{13}C NMR δ 172.80 (CCO), 153.58 (OCO), 80.06 ($(CH_3)_2C$), 64.11 (CH_2O), 52.54 (CH_3O), 24.57 ($(CH_3)_2C$), 14.18 (CH_3CH_2O); mass spectrum, *m/z* (relative intensity) 190 (M^+, 5), 159 (17), 131 (78), 101 (33), 86 (10), 73 (10), 59 (100).

Acknowledgment. This work has been financially supported by the Consiglio Nazionale delle Ricerche, Progetto Finalizzato "Chimica Fine e Secondaria".

Registry No. **1a**, 80675-53-2; **1b**, 65946-52-3; **1c**, 31469-15-5; **2a**, 90243-91-7; **2b**, 73689-70-0; **2c**, 30087-75-3; **3a**, 107010-02-6; **3b**, 107010-03-7; **3c**, 107010-05-9; **4a**, 33094-08-5; **4b**, 107010-04-8; **4c**, 30087-74-2; **5a**, 609-08-5; **5b**, 133-13-1; **5c**, 6065-55-0; **6b**, 107010-06-0.

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Preparation of Desmosterol from (20*S*,22*R*,*S*)-3β-Acetoxychola-5,23-dien-22-ol[1a]

Henry W. Kircher[1b] and Fumiko U. Rosenstein*

Department of Nutrition and Food Science, College of Agriculture, The University of Arizona, Tucson, Arizona 85721

Received August 26, 1986

Desmosterol (cholesta-5,24-dien-3β-ol) was originally synthesized by dehydration of 25-hydroxycholesterol but was considered to be 25-dehydrocholesterol at that time.[2]

(1) (a) Arizona Agricultural Experiment Station Journal, Ariticle 4258. (b) Deceased.

0022-3263/87/1952-2586$01.50/0 © 1987 American Chemical Society

Table I. Representative Reductions of 22-Dehydrodesmosterol and Its Acetate

$\Delta^{5,22E,24}$ derivative	catal. or reagent	solvent	time, h	ratio of products[a]
acetate	Raney Ni	EtOAc	18	cholesteryl acetate
acetate	Raney Ni	dioxane	18	1:2:4 Δ^5–$\Delta^{5,22}$–$\Delta^{5,24}$
sterol	Raney Ni	50:1 EtOAc–Et_3N	18	1:1:1 $\Delta^{5,22}$–$\Delta^{5,24}$–$\Delta^{5,22,24}$
sterol	$(Ph_3P)_3RhCl$	3:1 C_6H_6–EtOH	48	1:1:1 Δ^5–$\Delta^{5,22}$–$\Delta^{5,24}$
sterol	5% Rh/C	EtOAc	18	cholestanol
sterol[b]	$TsNHNH_2$	methoxyethanol	4.5	1:0.2:2:1 Δ^5–$\Delta^{5,22}$–$\Delta^{5,24}$–$\Delta^{5,22,24}$
sterol	NH_2NH_2, Cu^{2+}, air	5:1 diethylene glycol–HOAc	4	1:0.2:1:0.4 Δ^5–$\Delta^{5,22}$–$\Delta^{5,24}$–$\Delta^{5,22,24}$

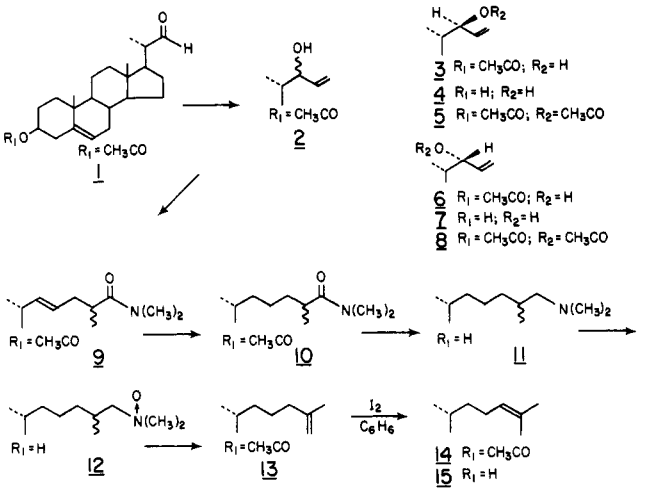
[a] Estimated by GC and/or TLC. [b] 33 mg of desmosteryl acetate isolated, mp 92.5–94 °C, from 250 mg of trienol.

It was subsequently prepared in an unambiguous manner by the Wittig reaction[3] and by dehydration of 25-hydroxycholesterol that avoided formation of the Δ^{25} isomer.[4] The 5,24- and 5,25-cholestadienyl acetates were separated by argentation column chromatography[5] and on $AgNO_3$-coated TLC plates;[5,6] their retention times by GC are almost identical.[5,7,8] Four other syntheses of desmosterol using organometallic reagents have been reported,[9-11] and in two others, no physical constants for the compound were reported.[12,13] In another case,[14] desmosterol was prepared from fucosterol.

In our hands, hydrogenation of 22-dehydrodesmosterol or its acetate[15] over Ni, Rh, Pd, and Pt in a number of solvents as well as homogeneous reduction over $(Ph_3P)_3RhCl$ and with diimide were insufficiently specific for the selective reduction of the Δ^{22} bond. Either no hydrogenation occurred (Raney Ni, pyridine) or it went too far to produce cholesterol or cholestanol (Ni or Rh, EtOAc) or, as in most cases, mixtures of Δ^5, $\Delta^{5,22}$, $\Delta^{5,24}$, and $\Delta^{5,22,24}$ derivatives were obtained from which desmosterol could be isolated only in low yield (Table I).

Isomerization of the $\Delta^{24(28)}$ bonds in fucosteryl and 24-methylenecholesteryl acetates to the $\Delta^{24(25)}$ position in ca. 50% yield by I_2 in benzene[16] suggested that a similar reaction of 25-dehydrocholesteryl acetate (**13**)[15] might be useful for the preparation of desmosterol. In this study, the starting material was (20*S*,22*R*,*S*)-3β-acetoxychola-5,23-dien-22-ol (**2**) prepared from (20*S*)-3β-acetoxybisnorchol-5-en-22-al (**1**) and vinylmagnesium bromide. Dropwise addition of vinylmagnesium bromide to (**1**) in THF on an ice bath was found to be the best condition for coupling with negligible attack on the 3β-acetoxy group and gave ca. 4:1 (by TLC) mixture of the 22*S* (**3**) and 22*R* (**6**) alcohol. This ratio was virtually unchanged by reaction temperatures ranging from −70 °C to ambient. The

Scheme I



epimeric alcohols were separated by column chromatography. The configurations of the less polar major alcohol (R_f 0.54, mp 163.5–165 °C, $[\alpha]^{25}_D$ −83.3°) and the more polar minor alcohol (R_f 0.48, mp 204–205 °C, $[\alpha]^{25}_D$ −37.4°) were determined by the Horeau method[17] and gave $[\alpha]^{25}_D$ −6.7°, optical yield 21%, and $[\alpha]^{25}_D$ +1.4°, 4.4%, respectively. The previous work for the configuration of C-22 alcohol by this method reported[18-21] that in many cases the *S* alcohol gave negative rotation and higher optical yield that the *R* alcohol. Accordingly, the configuration at C-22 of the less polar alcohol (**3**) is assigned as *S*,[22] and the more polar minor alcohol (**6**) receives the *R* configuration. Differentation of these two isomers was also reliably provided by ^{13}C NMR spectra. Reported[23] chemical shifts observed for (22*R*)- and (22*S*)-hydroxycholesteryl benzoate were also noted at C-17, C-20, C-21, C-23, and C-24 for the 22*R* and 22*S* alcohols. The mass spectra of these isomers are identical.

25-Dehydrocholesteryl acetate (**13**) was obtained from **2** in 69% yield by purification of only one intermediate (Scheme I). It rearranged smoothly to desmosteryl acetate (**14**) with I_2 in refluxing benzene to give ca. 9:1 ratio of the $\Delta^{5,24}/\Delta^{5,25}$ isomers. The same ratio was obtained from the $\Delta^{5,24}$ acetate. The two diene acetates were readily separated to give desmosteryl acetate in 83% yield.

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Experimental Section

Melting points were taken in vacuo, corrected. $[\alpha]^{25}_D$ values are measured in 3% in $CHCl_3$ unless otherwise stated. IR spectra were take in 2.5% in CS_2 or $CHCl_3$ and ^1H NMR spectra at 60 MHz in $CDCl_3$. ^{13}C NMR was recorded at 15 °C in $CDCl_3$ solution on a Bruker WM-250 Fourier transform spectrometer at 63 MHz. Chemical shifts (±0.1 ppm) are given with respect to Me_4Si, used as an internal standard. Mass spectra were taken with a Varian MAT 311A (direct inlet, 70 eV). t_r values of cholesteryl derivatives (5% OV-101, 250 °C) were as follows: Δ^0, 1.00; Δ^5, 1.00; $\Delta^{5,22E}$, 0.91; $\Delta^{5,24}$, 1.07; $\Delta^{5,25}$, 1.07; $\Delta^{5,22E,24}$, 1.14. R_f values of cholesteryl derivatives acetate (TLC system 1, 10% $AgNO_3$-silica gel plates, 5:2 hexane–benzene, 4-h development[15]) were as follows: Δ^0, 1.22; Δ^5, 1.00; $\Delta^{5,22E}$, 0.65; $\Delta^{5,24}$, 0.51; $\Delta^{5,22E,24}$, 0.28; $\Delta^{5,25}$, 0.17. R_f values of **2** acetoxy alcohols (TLC system 2, silica gel, 6:4 hexane–EtOAc one development) were as follows: **3**, 0.54; **6**, 0.48.

(20*S*,22*R*,*S*)-3β-Acetoxychola-5,23-dien-22-ol (2). Freshly prepared 0.97 M vinylmagnesium bromide[24] in 80 mL of THF was added dropwise over 10 min to a stirred solution of 18 g of **1** (mp 114–116.5 °C)[25] in 150 mL of THF on an ice bath. The mixture was stirred an additional 10 min and then poured into 200 mL of 1 N HCl. The products were extracted with ether, the ether layer was washed with H_2O, dried over Na_2SO_4, and evaporated, and the residue was chromatographed on Florisil with 3:1 CH_2Cl_2–petroleum ether (p.e.) to yield 12.8 g (66%) of **2** as a 22*R* and 22*S* mixture, single peak on GLC, t_r 0.91, two components on TLC (system 2), R_f 0.54 and 0.48 in a ratio of ca. 4:1.

(22*S*)-3β-Acetoxychola-5,23-dien-22-ol (3). The 22*R*,*S* mixture **2** was placed on 100 parts of 2:1 silica gel–Celite and eluted with 9:1 p.e.–ether and the R_f 0.54 material purified by crystallization from hexane: mp 163.5–165 °C, $[\alpha]^{25}_D$ −83.3°; IR 3610 (OH), 1730, 1240 (OAc), 1133, 1028, 980, 920, 840 cm^{-1}; ^1H NMR δ 0.70 (3 H, s, C18), 0.95 (3 H, d, C21), 1.02 (3 H, s, C19), 2.02 (3 H, s, CH_3CO), 2.32 (2 H, d, C4), 4.25 (1 H, br, C22), 4.70 (1 H, br, C3α), 5.02 and 5.19 (2 H, two q, C24), 5.32 (1 H, m, C6), 5.96 (1 H, octet, C23); ^{13}C NMR δ 52.17 (C17), 11.87 (C18), 40.98 (C20), 11.78 (C21), 74.28 (C22), 139.71 (C23), 113.62 (C24); mass spectra; *m*/*e* (relative intensity) 340 (M − HOAc, 49), 283 (M − HOAc − C_3H_5O, C20–C22 cleavage, 52), 80 (100), 159, 145, 133, 119, 107, 105, 95, 93, 91, 78, 67, 55, 44, and 43 (21–49). Anal. Calcd for $C_{26}H_{40}O_3$: C, 77.95; H, 10.06. Found: C, 77.86; H, 10.35.

Horeau analysis:[17] $[\alpha]^{25}_D$ −6.7° (C16, $CHCl_3$), 21% optical yield, 22*S*.

Acetoxy alcohol **3** was hydrolyzed to the 22*S* 3β,22-diol **4**, mp 205.5–206.5 °C (from acetone), $[\alpha]^{25}_D$ −99.5° (*c* 3, pyridine), and acetylated to the (22*S*) 3β,22-diacetate (**5**), mp 153–154.5 °C (from MeOH), $[\alpha]^{25}_D$ −83.6°.

(22*R*)-3β-Acetoxychola-5,22-dien-22-ol (6). When the 22*R*,*S* mixture **2** was crystallized from 5% benzene–hexane and ether, the more polar fraction, R_f 0.48, was concentrated in the crystals. Elution of this material from 300 parts of alumina with 9:1 p.e.–ether yielded **6**: mp 204–205 °C (from $CHCl_3$); $[\alpha]^{25}_D$ −37.4°; IR 3610 (OH), 1730, 1240 (OAc), 988, 922, 900 cm^{-1}; ^1H NMR similar to **3** except δ 0.97 (3 H, d, C21), 5.05 and 5.25 (2 H, two d, C24), 5.89 (1 H, octet, C23); ^{13}C NMR δ 52.95 (C17), 12.41 (C18), 41.86 (C20), 12.41 (C21), 74.84 (C22), 137.09 (C23), 116.20 (C24); mass spectra, identical with that of **3**. Anal. Calcd for $C_{26}H_{40}O_3$: C, 77.95; H, 10.06. Found: C, 77.86; H, 10.11.

Horeau analysis:[17] $[\alpha]^{25}_D$ +1.4° (*c* 18, $CHCl_3$), 4.5% optical yield, 22*R*.

Acetoxy alcohol **6** was hydrolyzed to the 22*R* 3β,22-diol **7**, mp 211.5–212.5 °C (from acetone), $[\alpha]^{25}_D$ −2.4° (*c* 3, pyridine), and acetylated to the 22*R* 3β,22-diacetate **8**, mp 173.5–174.5 °C (from MeOH), $[\alpha]^{25}_D$ −27.4°.

Hydrogenations of 22-Dehydrodesmosterol. Reduction of 100–300 mg of 22-dehydrodesmosterol or its acetate[15] with H_2 at room temperature was done in a flask over a magnetic stirrer attached to a hydrogen buret. Diimide reductions with hydrazine and *p*-tosyl hydrazide were at 80–110 °C. Samples were removed periodically for GC and acetylated, if necessary, for $AgNO_3$–silica gel TLC. Representative results of 38 experiments are given in Table I.

25-Dehydrocholesteryl Acetate (13). The previous preparation[15] was scaled-up and simplified. A solution of 10 g of **2** and 40 mL of 1-(dimethylamino)-1-methoxy-1-propene in 180 mL of benzene was refluxed under N_2 for 2 h and allowed to stand overnight. It was washed with water several times, dried over Na_2SO_4, and evaporated to dryness and the residue chromatographed on 350 g of 2:1 silica gel (Mallinckrodt, 100 mesh)–celite with 4:1 p.e.–ether to give 11.1 g (92%) of 25*R*,*S* $\Delta^{5,22}$ amide **9**, which was directly hydrogenated in 500 mL of EtOAc over 0.4 g of PtO_2 until H_2 absorption ceased. The catalyst and solvent were removed, and the residual Δ^5 amide **10** was dissolved in 160 mL of THF and added dropwise to a refluxing slurry of 8 g of $LiAlH_4$ in 250 mL of THF over 1 h. The mixture was refluxed an additional 30 min, most of the THF removed at atmospheric pressure, and the residue decomposed with moist ether and a minimal amount of water. The ether was decanted from the white $LiAl(OH)_4$ sludge and evaporated and the residual amine **11** refluxed directly with 18 mL of 30% H_2O_2 in 250 mL of MeOH overnight. The solution was evaporated in vacuo (<45 °C) to a syrup that was extracted with p.e. and was dried from 100% EtOH to leave 11.4 g of *N*-oxide **12** (theoretical yield, 11.1 g). It was dissolved in 300 mL of pyridine and pyrolyzed by stirring the solution with 10 g of KOH in 105 °C oil bath for 3.5 h. After removal of most of the pyridine in vacuo, the residue was mixed with 400 mL of 1 N HCl, and the product was extracted with ether and chromatographed on 500 g 2:1 silica gel–celite with 9:1 p.e.–ether to give 6.9 g of 25-dehydrocholesterol. This was acetylated (Ac_2O–py) and crystallized from MeOH to give 7.4 g of **13**, mp 111.5–113 °C (lit.[3-5,15] mp 112–114 °C), in 69% yield from **2**.

Desmosteryl Acetate (14). A solution of 4.00 g of **13** and 0.64 g of I_2 in 800 mL benzene was refluxed overnight, cooled, washed with 1% $Na_2S_2O_3$ and water, evaporated, and the residue was chromatographed on a 500 g of 20% $AgNO_3$ 2:1 silica gel–celite column with 3:7 benzene–hexane to yield 3.33 g (83%) of **14**, 0.08 g of mixed fractions, and 0.47 g (11%) of **13**. **14**: mp 94–95 °C (from MeOH), $[\alpha]^{25}_D$ −42.4° (lit. 92.5–93 °C, −40.6°;[4] 96–97 °C, −43°[5]).

Desmosterol (15). Acetate **14** was hydrolyzed and desmosterol crystallized from MeOH: mp 121.5–122.5 °C, $[\alpha]^{26}_D$ −38.5° (lit. 120.5–121 °C, −39.2°;[4] 121–122 °C, −41°[5]).

Acknowledgment. We thank Dr. Robert Bates, Chemistry Department, University of Arizona, for assistance with ^{13}C NMR spectra and the National Science Foundation (Grant DEB-8207056) for partial support of this work.

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Synthesis of Fluoro Ethers with Acetyl Hypofluorite

David Hebel and Shlomo Rozen*

School of Chemistry, Raymond and Beverly Sackler Faculty of Exact Sciences, Tel-Aviv University, Tel-Aviv 69978, Israel

Received October 31, 1986

Since its first synthesis about six years ago, acetyl hypofluorite (AcOF) has become a popular fluorinating agent.[1] Its developing chemistry includes reactions with aromatic mercury derivatives including estrone[2] and also simple aromatic compouds, using particularly AcO^{18}F for

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0022-3263/87/1952-2588$01.50/0 © 1987 American Chemical Society