Beckmann Rearrangement of Δ^4-6-Hydroxyimino Steroids

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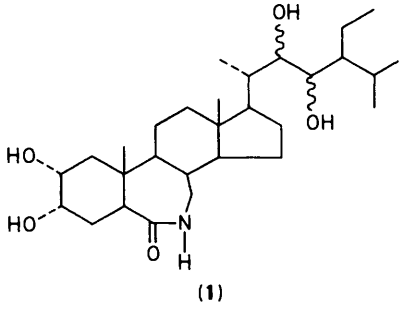
Beckmann rearrangement of Δ^4-6-hydroxyimino steroids gave solely the products of vinyl migration. Compounds having a 3-hydroxy or 3-acetoxy group suffer elimination of the substituent during the reaction.

In the course of work directed towards the synthesis of (2*R*,3*S*,22*S*,23*S*)- and (2*R*,3*S*,22*R*,23*R*)-2,3,22,23-tetrahydroxy-B-homo-7-aza-5α-stigmastan-6-one (**1a** and **b**), two aza analogues of homobrassinolide, a plant-growth-promoting sterol, we[1] and others[2] observed that saturated 6-hydroxyimino-5α-steroids possess an *anti* configuration of the oxime group, and by Beckmann rearrangement give 6-azalactams, *e.g.* (2*R*,3*S*,22*S*,23*S*)- and (2*R*,3*S*,22*R*,23*R*)-2,3,22,23-tetrahydroxy-B-homo-6-aza-5α-stigmastan-7-one (**2a** and **b**).

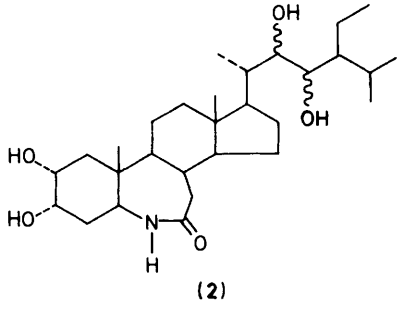
Since Ahmad *et al.* reported[3] that (3*S*)-3-acetoxy-6-hydroxyiminostigmast-4-ene (**3a**) undergoes Beckmann rearrangement to afford (3*S*)-3-acetoxy-B-homo-7-azastigmast-4-en-6-one (**4a**), we have attempted the synthesis of lactam (**1a**)† starting from (3*S*,22*S*,23*S*)-3,22,23-triacetoxy-6-hydroxyiminostigmast-4-ene (**3b**) which, by Beckmann rearrangement, should afford[3] the (3*S*,22*S*,23*S*)-3,22,23-triacetoxy-B-homo-7-azastigmast-4-en-6-one (**4b**). However, all efforts to rearrange the hydroxyimino compound (**3b**) to the lactam (**4b**) by Beckmann rearrangement were unsuccessful, although a variety of experimental procedures and conditions was further examined. This finding prompted us to re-examine the Beckmann rearrangement of the hydroxyimino compound (**3a**). Using thionyl chloride–alkali,[3,4] or phosphorus pentachloride for the rearrangement,[5] only complex mixtures of inseparable compounds were obtained. They showed, as a common feature, the loss of the acetoxy group (^{1}H n.m.r., and i.r. evidence). Treatment of the hydroxyimino steroid (**3a**) with toluene-*p*-sulphonyl chloride followed by chromatography on alumina[6] afforded a lactam, assigned the structure B-homo-6-azastigmasta-2,4-dien-7-one (**5a**), as the sole identifiable product, in low yield. Since these conditions are known to affect the Beckmann rearrangement without isomerization of the hydroxyimino compound prior to the stereospecific *trans* migration of the *anti* carbon,[7,8] we thought that conditions involving a fast geometrical interconversion between *syn* and *anti* *p*-tolylsulphonyloxyimino compounds in polar solvents, and preferential rearrangement of the *syn* isomers,[9,10] would favour the formation of the lactam (**4a**) derived from migration of the 7-alkyl substituent. However, also under these conditions (treatment with hydrochloric acid in acetic acid),[9,10] the only isolated compound was the lactam (**5a**) derived from regiospecific migration of the vinylic C-5 of compound (**3a**) and loss of the elements of acetic acid. The same lactam (**5a**) was obtained in a more convenient yield by rearrangement of the hydroxyimino compound (**3a**) with trimethylsilyl polyphosphate (PPSE).[11] Analogous results were obtained for reaction with the hydroxyimino compound (**3b**), which afforded (22*S*,23*S*)-22,23-diacetoxy-B-homo-6-azastigmasta-2,4-dien-7-one (**5b**); with (3*S*)-3-acetoxy-6-hydroxyiminocholest-4-ene (**3c**), (3*S*)-6-hydroxyiminocholest-4-en-3-ol (**3d**), and 6-

† For the synthesis of this compound, see preceding paper.

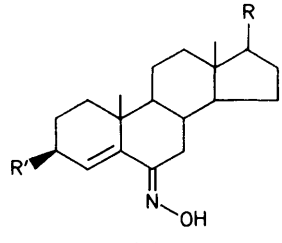


(1)

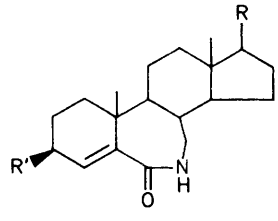
a; 22*S*, 23*S*
b; 22*R*, 23*R*



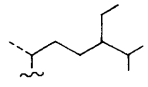
(2)

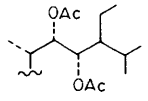


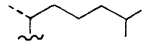
(3)

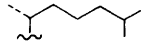


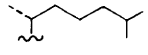
(4)

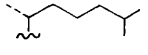
a; R =  , R' = OAc

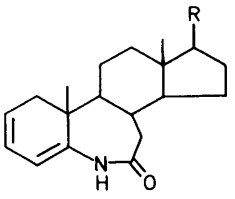
b; R =  , R' = OAc

c; R =  , R' = OAc

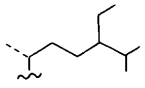
d; R =  , R' = OH

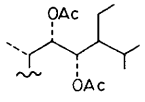
e; R =  , R' = H, Δ^2

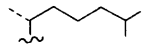
f; R =  , R' = H

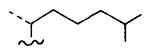


(5)

a; R = 

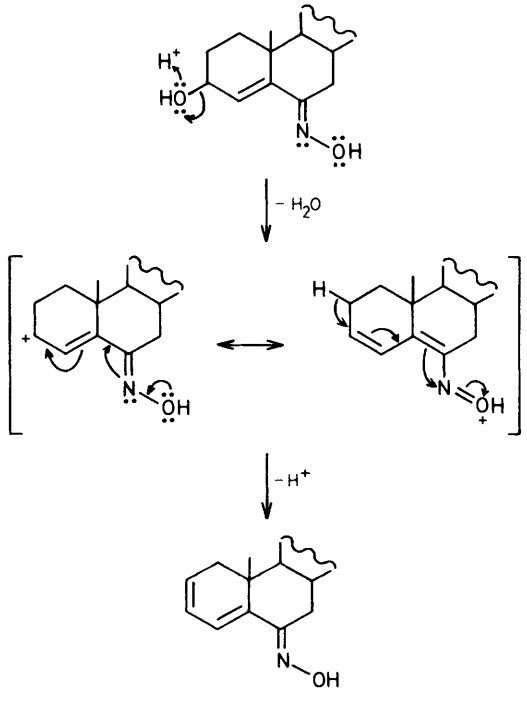
b; R = 

c; R = 

d; R =  , 2,3-dihydro

hydroxyiminocholesta-2,4-diene (**3e**), all of which afforded B-homo-6-azacholesta-2,4-dien-7-one (**5c**); and with 6-hydroxyiminocholest-4-ene (**3f**) which afforded B-homo-6-azacholest-4-en-7-one (**5d**). All these results show that in these cases the olefinic group migrates more efficiently than the alkyl group under *syn–anti* equilibration conditions.

The migration of the olefinic group was, on the other hand, favoured by the *anti* stereochemistry of all hydroxyimino compounds studied. The *anti* stereochemistry was derived from the ^{1}H n.m.r. spectra, which show a one-proton signal shifted downfield (δ *ca.* 3.3) as a double doublet. Clearly, the proton responsible for this signal suffers an anisotropic effect of the oxygen atom of the hydroxyimino group.[12] The high-field position (δ *ca.* 5.75) of the signal attributable to the olefinic proton at C-4 indicates that it is less deshielded by the hydroxyimino group than by the parent ketone group (usually at δ *ca.* 6.1). Models show that a steric arrangement responsible for this pattern of signals exists in the *anti* configuration of the hydroxyimino compounds and that the proton influenced by the anisotropic effect of the oxygen is the 7β-equatorial one, estimated to be *ca.* 2.4 Å from the hydroxyimino oxygen.



Scheme.

The structure of the lactams (**5a**—**d**) was in agreement with their physico-chemical properties (elemental analysis, i.r., u.v., and ^{1}H n.m.r.). In particular the ^{1}H n.m.r. spectra were diagnostic for 6-aza-7-oxo lactams, showing in all cases the expected resonances for the methylene protons adjacent to amide carbonyl,[7] usually between δ 2.3—2.4, and the absence of signals attributable to methylene protons adjacent to amide nitrogen, generally at δ *ca.* 3.4.

As final confirmation of the structure of compounds (**5a**, **c**, and **d**) they were reduced to saturated lactams identical with those obtained by Beckmann rearrangement of the corresponding saturated 6-hydroxyimino steroids.

The loss of the elements of acetic acid or of water in the rearrangement of hydroxyimino compounds (**3a**—**d**) may be rationalized considering that the elimination of the 3β-hydroxy or 3β-acetoxy group (Scheme) affords a highly stabilized carbonium ion which collapses to the di-unsaturated hydroxyimino compound. This reaction has a precedent[13] in the loss of hydrobromic acid in the preparation of the hydroxyimino derivative of 6β-bromocholest-4-en-3-one.

Experimental

Conditions and equipment used in the synthesis were those described in the preceding paper. Cholesta-2,4-dien-6-one was prepared according to reference 14; (3*S*)-3-acetoxycholest-4-en-6-one was prepared according to reference 15 and the corresponding alcohol, m.p. 147—149 °C (from methanol), was prepared by saponification.

Preparation of Hydroxyimino Compounds: General Procedure.—Hydroxylamine hydrochloride (500 mg) and anhydrous sodium acetate (500 mg) were dissolved in aqueous ethanol (100 ml; 50%) and combined with a saturated solution of the corresponding ketone (1 g) in absolute ethanol. The solution was kept for 24 h at room temperature. The solvent was then removed under reduced pressure without heating. Dilution with water, extraction (Et_2O), drying, and evaporation afforded the hydroxyimino compound as a solid cake. Crystallization or column chromatography afforded the pure hydroxyimino compound in 70—75% yields.

(3S)-3-*Acetoxy*-6-*hydroxyiminostigmast*-4-*ene* (**3a**) had m.p. 162—163 °C (from methanol) (lit.,[3] 160 °C); $\nu_{max.}$ 3 260, 1 730, 1 650, and 1 250 cm^{-1}; δ 0.70 (3 H, s), 1.01 (3 H, s), 2.03 (3 H, s, OAc), 3.4 (1 H, dd, *J* 4 and 12 Hz, 7β-H), 5.35 (1 H, m, $w_{\frac{1}{2}}$ 13 Hz, 3-H), 5.75 (1 H, br s, $w_{\frac{1}{2}}$ 4 Hz, 4-H), and 8.90 (1 H, m, NOH) (Found: C, 76.5; H, 10.6; N, 2.95. Calc. for $C_{31}H_{51}NO_7$: C, 76.65; H, 10.6; N, 2.9%). All these physicochemical properties were identical with those reported.[3]

(3S,22S,23S)-3,22,23-*Triacetoxy*-6-*hydroxyiminostigmast*-4-*ene* (**3b**) had m.p. 117—120 °C (from methanol; sintered at 115 °C); $\nu_{max.}$ 3 260, 1 730, 1 650, and 1 230 cm^{-1}; δ 0.68 (3 H, s), 0.90 (3 H, s), 2.04 (6 H, s, 2 × OAc), 2.08 (3 H, s, AcO), 3.30 (1 H, dd, *J* 4 and 12 Hz, 7β-H), 5.02 (1 H, m, 22- or 23-H), 5.28 (2 H, m, $w_{\frac{1}{2}}$ 14 Hz, overlapping, 3- and 23- or 22-H), 5.7 (1 H, br s, $w_{\frac{1}{2}}$ 4 Hz, 4-H), and 8.3 (1 H, m, NOH) (Found: C, 70.0; H, 9.2; N, 2.3. $C_{35}H_{55}NO_7$ requires C, 69.85; H, 9.2; N, 2.3%).

(3S)-3-*Acetoxy*-6-*hydroxyiminocholest*-4-*ene* (**3c**) had m.p. 97—98 °C (amorphous); $\nu_{max.}$ 3 580, 3 320, 1 720, 1 650, and 1 250 cm^{-1}; δ 0.70 (3 H, s), 0.90 (3 H, s), 2.02 (3 H, s, AcO), 3.30 (1 H, dd, *J* 4 and 12 Hz, 7β-H), 5.30 (1 H, m, $w_{\frac{1}{2}}$ 13 Hz, 3-H), 5.70 (1 H, br s, $w_{\frac{1}{2}}$ 4 Hz, 4-H), and 8.8 (1 H, m, NOH) (Found: 76.1; H, 10.4; N, 3.1. $C_{29}H_{47}NO_3$ requires C, 76.1; H, 10.35; N, 3.05%).

(3S)-6-*Hydroxyiminocholest*-4-*en*-3-*ol* (**3d**) had m.p. 138—139 °C (from methanol); $\nu_{max.}$ 3 850, 3 300, and 1 650 cm^{-1}; δ

0.68 (3 H, s), 0.90 (3 H, s), 3.30 (1 H, dd, *J* 4 and 12 Hz, 7β-H), 4.15 (1 H, m, $w_{\frac{1}{2}}$ 13 Hz, 3-H), 5.80 (1 H, br s, $w_{\frac{1}{2}}$ 4 Hz, 4-H), and 6.35 (2 H, m, overlapping, OH and NOH) (Found: C, 78.1; H, 11.0; N, 3.4. $C_{27}H_{45}NO_2$ requires C, 78.0; H, 10.9; N, 3.4%).

6-*Hydroxyiminocholesta*-2,4-*diene* (**3e**) had m.p. 146—149 °C (decomp., amorphous); $\nu_{max.}$ 3 580, 3 280, 1 640, and 1 620 cm^{-1}; $\lambda_{max.}$ (EtOH) 300 nm (ε 7 500); δ 0.73 (3 H, s), 0.93 (6 H, s, overlapping), 3.35 (1 H, dd, *J* 4 and 12 Hz, 7β-H), 5.9 (2 H, m, $w_{\frac{1}{2}}$ 8 Hz, overlapping, 3- and 4-H), 6.35 (1 H, m, $w_{\frac{1}{2}}$ 8 Hz, 2-H), and 9.4 (1 H, m, NOH) (Found: C, 81.6; H, 10.8; N, 3.45. $C_{27}H_{43}NO$ requires C, 81.55; H, 10.9; N, 3.5%).

6-*Hydroxyiminocholest*-4-*ene* (**3f**) had m.p. 147—150 °C (decomp., amorphous) (lit.,[14] 150—165 °C); $\nu_{max.}$ 3 580, 3 240, and 1 650 cm^{-1}; δ 0.75 (3 H, s), 0.90 (3 H, s), 3.35 (1 H, dd, *J* 4 and 12 Hz, 7β-H), 5.7 (1 H, m, $w_{\frac{1}{2}}$ 6 Hz, 4-H), and 9.4 (1 H, m, NOH) (Found: C, 81.15; H, 11.2; N, 3.5. $C_{27}H_{45}NO$ requires C, 81.1; H, 11.35; N, 3.5%).

Preparation of p-*Tolylsulphonyloxyimino Compounds.*—The hydroxyimino compound (1 g) and toluene-*p*-sulphonyl chloride (830 mg) were dissolved in trichloromethane (20 ml) and the solution was treated with aqueous sodium hydroxide (20 ml of a 15% solution). After being stirred for 2 h, the mixture was poured in cold water, and extracted (Et_2O), and the extract was washed with water, dried, and evaporated under reduced pressure. Purification of the intermediates was not practicable and they were used directly in the Beckmann rearrangement without purification.

Beckmann Rearrangement.—(a) *Of hydroxyimino compounds with trimethylsilyl polyphosphate.* The procedure of Imamamoto *et al.* was used.[11] The hydroxyimino compound (1.49 mmol) was dissolved in a tetrachloromethane solution (4.5 ml) of PPSE and the mixture was stirred at room temperature for 2 h. [PPSE was prepared by dissolving phosphorus pentaoxide (10 g) in a refluxing mixture of hexamethyldisiloxane (21 ml) and tetrachloromethane (40 ml) for 1.5 h.] Usual work-up, followed by rapid chromatography (60% ethyl acetate in hexane), afforded the lactam.

(b) *Of* p-*tolylsulphonyloxyimino compounds with hydrochloric acid.* A crude *p*-tolylsulphonyloxyimino compounds from the foregoing preparation (1 g) was dissoved in acetic acid (10 ml) and then conc. hydrochloric acid was added (1 ml). After 2 min the reaction mixture was poured into aqueous sodium carbonate and extracted with ethyl acetate. Usual work-up and rapid chromatography (30% ethyl acetate in hexane) afforded the lactam. The following lactams were thus prepared.

B-*Homo*-6-*azastigmasta*-2,4-*dien*-7-*one* (**5a**) was obtained from oxime (**3a**) in 60 [procedure (a)] and 70% [(b)] yield, $\nu_{max.}$ 3 390, 1 655, and 1 585 cm^{-1}; $\lambda_{max.}$ (EtOH) 273 nm (ε 7 800); δ 0.64 (3 H, s), 0.99 (3 H, s), 2.43 (2 H, m, $w_{\frac{1}{2}}$ 10 Hz, 7a-H_2), 5.8 (3 H, m, $w_{\frac{1}{2}}$ 6 Hz, overlapping, 2-, 3-, and 4-H), and 8.15 (1 H, m, NH) (Found: C, 81.9; H, 11.0; N, 3.3. $C_{29}H_{47}NO$ requires C, 81.8; H, 11.1; N, 3.3%). The lactam decomposes on exposure to light or air.

(22S,23S)-22,23-*Diacetoxy*-B-*homo*-6-*azastigmasta*-2,4-*dien*-6-*one* (**5b**) was obtained from oxime (**3b**) in 60 [(a)] and 65% [(b)] yield. It was a glass, with $\nu_{max.}$ 3 390, 1 730, 1 655, 1 585, and 1 255 cm^{-1}; $\lambda_{max.}$ (EtOH) 273 nm (ε 7 800); δ 0.69 (3 H, s), 0.9 (3 H, s), 2.0 (3 H, s, AcO), 2.02 (3 H, s, AcO), 2.30 (2 H, m, $w_{\frac{1}{2}}$ 13 Hz, 7a-H_2), 5.03 (1 H, m, $w_{\frac{1}{2}}$ 9 Hz, 22- or 23-H), 5.25 (1 H, m, $w_{\frac{1}{2}}$ 9 Hz, 23- or 22-H), 5.8 (3 H, m, $w_{\frac{1}{2}}$ 6 Hz, overlapping, 2-, 3-, and 4-H), and 8.15 (1 H, m, NH) (Found: C, 73.3; H, 9.4; N, 2.6. $C_{33}H_{51}NO_5$ requires C, 73.2; H, 9.5; N, 2.6%). The lactam decomposes on exposure to light or air.

B-*Homo*-6-*azacholesta*-2,4-*dien*-7-*one* (**5c**) was obtained from compounds (**3c**), (**3d**), and (**3e**) in 75% yield [(a) and (b)]. It had m.p. 144—147 °C (from acetone); $\nu_{max.}$ 3 390, 1 655, 1 585, and 1 255 cm^{-1}; $\lambda_{max.}$ (EtOH) 273 nm (ε 7 800); δ 0.65 (3 H, s), 0.99 (3 H, s), 2.43 (2 H, m, $w_{\frac{1}{2}}$ 10 Hz, 7a-H_2), 5.8 (3 H, m, $w_{\frac{1}{2}}$ 6 Hz, overlapping, 2-, 3-, and 4-H), and 8.15 (1 H, m, NH) (Found: C, 81.5; H, 10.9; N, 3.6. $C_{27}H_{43}NO$ requires C, 81.55; H, 10.9; N, 3.5%). The lactam decomposes on exposure to light or air.

B-*Homo*-6-*azacholest*-4-*en*-7-*one* (**5d**) was obtained from oxime (**3f**) in 65% yield [(a) and (b)]. It had m.p. 145—147 °C (amorphous); $\nu_{max.}$ 3 380 and 1 642 cm^{-1}; δ 0.69 (3 H, s), 0.90 (3 H, s), 2.3 (2 H, m, $w_{\frac{1}{2}}$ 12 Hz, 7a-H_2), 5.58 (1 H, m, $w_{\frac{1}{2}}$ 8 Hz, 4-H), and 8.1 (1, m, NH) (Found: C, 81.2; H, 11.2; N, 3.5. $C_{27}H_{45}NO$ requires C, 81.1; H, 11.35; N, 3.5%).

B-*Homo*-6-*aza*-5α-*stigmastan*-7-*one.*—(a) *By catalytic reduction of lactam* (**5a**). The lactam (**5a**) (100 mg) was dissolved in acetic acid (20 ml) and hydrogenated for 12 h in the presence of platinum dioxide. Filtration and work-up afforded, after rapid chromatography, B-homo-6-aza-5α-stigmastan-7-one (60 mg), m.p. 153—155 °C (from moist acetone); $\nu_{max.}$ 3 380 and 1 665 cm^{-1}; δ 0.69 (3 H, s), 0.9 (3 H, s), 2.25 (2 H, m, $w_{\frac{1}{2}}$ 10 Hz, 7a-H_2), 3.4 (1 H, m, $w_{\frac{1}{2}}$ 20 Hz, 5α-H), and 6.0 (1 H, m, NH) (Found: C, 81.0; H, 11.0; N, 3.3. $C_{29}H_{51}NO$ requires C, 81.05; H, 11.2; N, 3.25%).

(b) *By Beckmann rearrangement of* 6-*hydroxyimino*-5α-*stigmastane.* 6-Hydroxyimino-5α-stigmastane (500 mg) was dissolved in thionyl chloride (5 ml; purified immediately before use by distillation from quinoline and from raw linseed oil) at 0 °C. After 30 min the solution was poured into aqueous potassium hydroxide (55 ml; 4M) at 20 °C, and the product was extracted with diethyl ether. Crystallization from moist acetone afforded B-*homo*-6-*aza*-5α-*stigmastan*-7-*one* (270 mg), m.p. 153—155 °C (Found: C, 81.1; H, 11.9; N, 3.1. $C_{29}H_{51}NO$ requires C, 81.05; H, 12.0; N, 3.25%). All other physico-chemical properties were identical with those reported above.

B-*Homo*-6-*aza*-5α-*cholestan*-7-*one.*—(a) *By catalytic reduction of lactam* (**5c**). The lactam (**5c**) (100 mg) was dissolved in acetic acid (20 ml) and hydrogenated for 12 h in the presence of platinum dioxide. Filtration and evaporation left a residue which, after crystallization from ethanol, yield 60 mg, had m.p. 175—176 °C; $[\alpha]_D^{20}$ +52° (lit.,[3] m.p. 175—176 °C; $[\alpha]_D^{20}$ +52°); $\nu_{max.}$ (EtOH) 3 400 and 1 665 cm^{-1}; δ 0.69 (3 H, s), 0.90 (3 H, s), 2.25 (2 H, m, $w_{\frac{1}{2}}$ 10 Hz, 7a-H_2), 3.4 (1 H, m, $w_{\frac{1}{2}}$ 20 Hz, 5α-H), and 5.6 (1 H, m, NH) (Found: C, 80.6; H, 11.7; N, 3.5. Calc. for $C_{27}H_{47}NO$: C, 80.7; H, 11.8; N, 3.5%).

(b) *By Beckmann rearrangement of* 6-*hydroxyimino*-5α-*cholestane.* A solution of 6-hydroxyimino-5α-cholestane (550 mg) in thionyl chloride was treated as described above for the stigmastane homologue. Crystallization from ethanol afforded B-homo-6-aza-5α-cholestan-7-one (300 mg), m.p. 175—176 °C (Found: C, 80.7; H, 11.75; N, 3.6. Calc. for $C_{27}H_{47}NO$: C, 80.7; H, 11.8; N, 3.5%). All other physicochemical properties were identical with those reported above.

Synthesis of (3S,22S,23S)-3,22,23-*Triacetoxystigmast*-4-*en*-6-*one.*—A solution of (3S,22S,23S)-3,22,23-*triacetoxy*-5-*bromo*-5α-*stigmastan*-6-*one* [m.p. 181—182 °C (from methanol); δ 0.65 (3 H, s, 18-H_3), 1.06 (3 H, s, 19-H_3), 2.01 (3 H, s, AcO), 2.03 (3 H, s, AcO), 2.07 (3 H, s, AcO), 5.10 (1 H, m, 22- or 23-H), and 5.20—5.40 (2 H, m, overlapping, 3-H and 23- or 22-H) (Found: C, 62.9; H, 8.2. $C_{35}H_{55}BrO_7$ requires C, 62.95; H, 8.3%)] (1 g), (prepared by bromination[16] of (3*S*,22*S*,23*S*)-3,22,23-triacetoxy-5α-stigmastan-6-one[17]), sodium hydrogen carbonate (1 g), and dimethyl sulphoxide (10 ml) was heated at 130 °C for 1.5 h. Usual work-up and crystallization afforded (3S,22S,23S)-3,22,23-*triacetoxystigmast*-4-*en*-6-*one* (750 mg), m.p. 178—179 °C (from methanol); $\lambda_{max.}$ (EtOH) 238 nm (ε 6 800); $\nu_{max.}$ 1 730, 1 690, 1 635, and 1 250 cm^{-1}; δ 0.69 (3 H, s,

18-H_3), 1.00 (3 H, s, 19-H_3), 2.01 (6 H, s, 2 × AcO), 2.07 (3 H, s, AcO), 5.00 (1 H, m, 22- or 23-H), 5.20—5.40 (2 H, m, overlapping, 3-H and 23- or 22-H), and 6.10 (1 H, br s, $w_{\frac{1}{2}}$ 4 Hz, 4-H) (Found: C, 71.5; H, 9.4. $C_{35}H_{54}O_7$ requires C, 71.6; H, 9.3%).

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