Base-catalysed Fragmentation of 5,6β-Epoxy-3β-hydroxy-5β-cholestan-19-al

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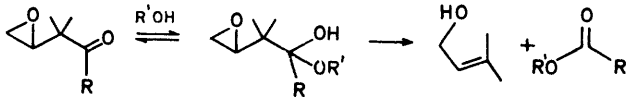
Under basic conditions, 5,6β-epoxy-3β-hydroxy-5β-cholestan-19-al (1) underwent fragmentative elimination of the 10β-function, whereas the isomeric 5α,6α-epoxide (9) underwent diaxial opening of the epoxy-group. The ^{1}H n.m.r. spectrum of the 5β,6β-epoxide (1) and the reactivity of its 3β-methoxy-derivative (4) indicate that the fragmentation involves chelation between an intramolecular 3,19-hemiacetal (22) and the epoxide oxygen, with a chair-like transition state. The products obtained from the acid-catalysed and thermal reactions of the 5β,6β-epoxide (1) similarly implicate the intramolecular hemiacetal (22).

We have been examining reactions in which the elimination of the steroidal C-10, in various oxidation states, is initiated by the opening of a 5β,6β-epoxide [1] or of a 4β,5β-epoxide.[2] In this connection, an earlier report [3] that 5,6β-epoxy-3β-hydroxy-5β-cholestan-19-al (1) undergoes a fragmentative elimination of the 10β-formyl group in the presence of base was viewed with interest.

In general, the fragmentation of β,γ-epoxy-carbonyl compounds (Scheme 1) is most commonly encountered [4] under conditions where the carbonyl group can exist as an acetal and fragmentation is initiated by the Lewis acid-catalysed opening of the epoxide.



Scheme 1

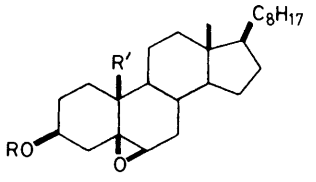
The base-catalysed version of this reaction is much less common. In fact, aside from the above example, the only other report of this type of fragmentation reaction that we are aware of is that observed [5] with epoxycyclobutanones, *e.g.* (12). In this latter case, the release of strain energy [6] in the rings incorporating the respective electrofugal and nucleofugal fragments is undoubtedly an important activating feature. The base-catalysed fragmentation of the epoxy-steroid (1) may therefore be considered somewhat unusual since activation for the cleavage of the electrofugal fragment does not seem to be present. Accordingly, we re-examined the reaction of (1) along with some related steroidal epoxyaldehydes to see what factors may be involved.

The epoxy-aldehyde (1) and its 5α,6α-isomer (9) were prepared by careful hydrolysis of the respective 3β-acetates (2) and (10), which in turn were obtained by oxidation of the alcohols (3) and (11). The epoxy-aldehydes (1) and (9) were chromatographically homogeneous and crystallised readily from methanol. Good analytical data were obtained for (1), but those for (9) indicated the presence of a hydrate. However, both compounds exhibited broad melting ranges, specific rotations which changed with time, and ^{1}H n.m.r. spectra which were anomalous in view of the functionality present. These features were attributed to slow equilibration between the hydroxy-aldehyde form of (1) or (9) and the intramolecular hemiacetal (22) or (13). This process was most evident from the ^{1}H n.m.r. spectra of (1) (see Figure). In deuteriochloroform, a freshly prepared sample exhibited a spectrum consistent with a *ca.* 2 : 1 mixture of (1) and (22). This changed until a *ca.* 1 : 1 mixture was established after 20 h. The hydrogen atoms of the hemiacetal function of (22) are observed as a distinct AB quartet, indicative of a strong hydrogen bond to the epoxide oxygen. This latter feature is similar to that observed [7] with the 19-hydroxy-5β,6β-epoxide (3). In the present case, the 12 Hz coupling constant for the vicinal H–O–C–H system corresponds to a *ca.* 180° torsion angle.[7]

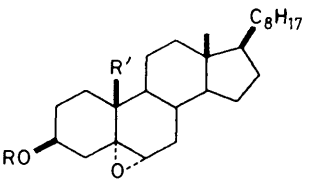
When a methanolic solution of the 5β,6β-epoxide (1) containing aqueous potassium hydroxide was heated at reflux for 36 h, the fragmentation product (14) was obtained in 78% yield. Under these conditions, the isomeric 5α,6α-epoxide (9) afforded a complicated mixture of products which were left unidentified. The reaction of the latter epoxide was somewhat cleaner with methanolic potassium hydroxide, and a quantity of the major product, the 6β-methoxide (17), was isolated. Evidently, the fragmentation reaction is unique to the 5β,6β-epoxide (1); *trans*-diaxial opening of the epoxide would involve attack at the tertiary 5-position and is therefore not favoured.

Upon examining the reaction of the 5β,6β-epoxide (1) with different bases, it was found that magnesium methoxide was dramatically more effective [90% yield of the allylic alcohol (14) after 0.3 h] in promoting the fragmentation reaction than sodium methoxide [57% yield of (14) after 142 h]. Since the magnesium cation would be a more effective Lewis acid and the products of epoxide solvolysis were not detected, the above observation was taken to indicate that chelation [5] between the *syn*-oriented electrofugal and nucleofugal fragments may be important in this reaction.

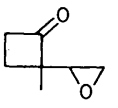
To see if the intramolecular hemiacetal (22) was involved in the fragmentation process, the base-catalysed reactions of the 3β-methoxy-derivative (4) were examined. This compound was prepared from the 19-t-butyldimethylsilyl ether (5) *via* a sequence involving: hydrolysis of the 3β-acetate (5), methylation of the 3β-



(1) R = H, R′ = CHO
(2) R = Ac, R′ = CHO
(3) R = Ac, R′ = CH_2OH
(4) R = Me, R′ = CHO
(5) R = Ac, R′ = $CH_2OSiMe_2Bu^t$
(6) R = H, R′ = $CH_2OSiMe_2Bu^t$
(7) R = Me, R′ = $CH_2OSiMe_2Bu^t$
(8) R = Me, R′ = CH_2OH



(9) R = H, R′ = CHO
(10) R = Ac, R′ = CHO
(11) R = Ac, R′ = CH_2OH



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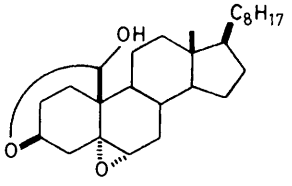

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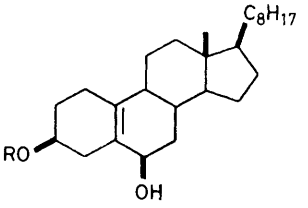
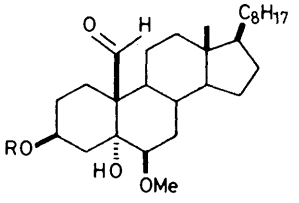
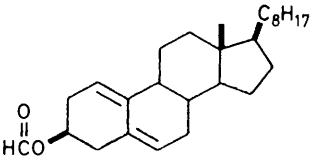


(14) R = H
(15) R = Me
(16) R = CHO



(17) R = H
(18) R = Ac



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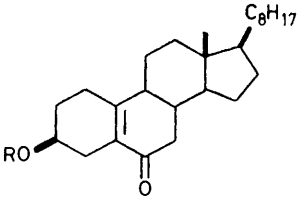


(20) R = CHO
(21) R = H

alcohol (6), desilylation of the 3β-methoxy-compound (7), and oxidation of the 19-alcohol (8). With aqueous potassium hydroxide in methanol, the 3β-methoxy compound (4) underwent fragmentation more slowly [49% yield of the allylic alcohol (15) after 108 h; 30% recovery of starting material] than the 3β-hydroxy-compound (1). With magnesium methoxide, the 19-alcohol (8) was obtained [56% yield after 97 h; 35% recovered starting material] instead of a fragmentation product. Evidently, a Meerwein–Pondorf–Verley-type reduction [8] occurs when the formation of an intramolecular hemiacetal is no longer possible.

These observations indicate that the base-catalysed fragmentation reaction proceeds most readily *via* a chelated intramolecular hemiacetal. Such an intermediate would be expected to resemble the intramolecular hemiacetal (22), where there is a strong hydrogen bond to the epoxide oxygen. In this latter case, the ring, formed in part by the hydrogen bond, closely approximates to the chair conformation of cyclohexane.

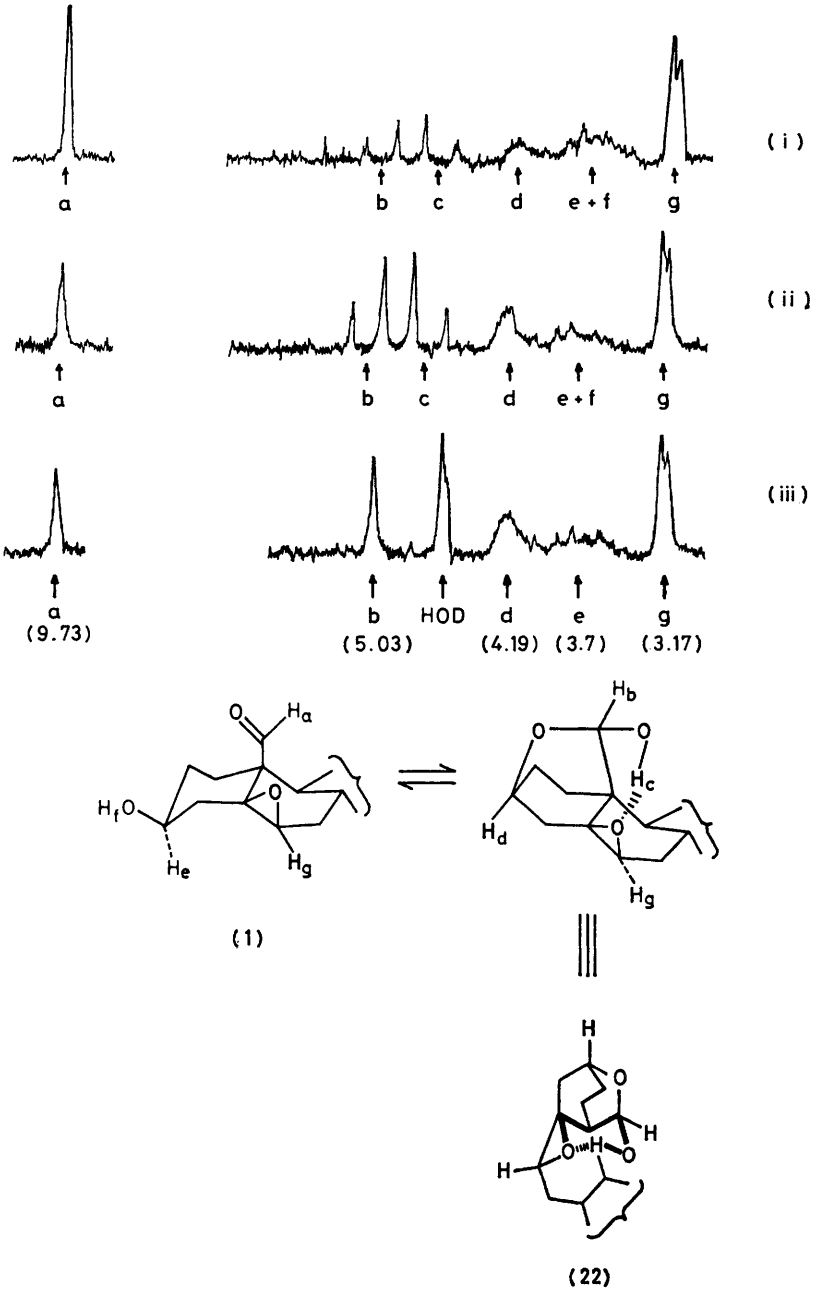
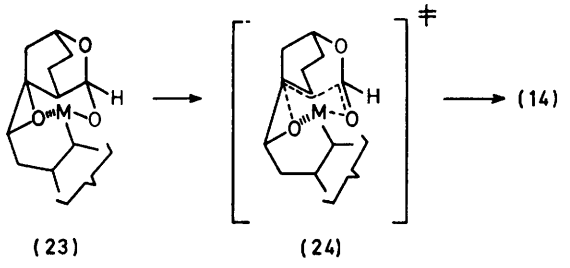


FIGURE 60 MHz ^{1}H N.m.r. spectrum of (1) (i) after 5 min, integration (total 4.1 H), a : (b + c) : (d + e + f) : g 0.7 : 0.9 : 1.5 : 1; (ii) after 20 h, integration (total 4.0 H), a : (b + c) : (d + e + f) : g 0.4 : 1.1 : 1.5 : 1; δ_b 5.05, δ_c 4.72, J_{bc} 12 Hz; (iii) after D_2O addition, integration (total 3.1 H), a : b : (d + e): g, 0.4 : 0.5 : 1.2 : 1

Since chair-like transition states have been postulated [9] for a number of pericyclic reactions which involve a chelating species, it is suggested that the base-catalysed fragmentation of (1) follows a similar course.

This being the case, the ready formation of an intermediate (23) which closely resembles the transition state (24) of the fragmentation process would significantly lower the activation energy of this reaction. It would then be this feature of the epoxy-aldehyde (1) which facilitates the fragmentation reaction. Chelation allows this reaction to proceed even though the electrofugal and nucleofugal fragments are disposed in a synclinal fashion and would thereby distinguish this process from that normally encountered in a Grob-type fragmentation [10] where stereoelectronic factors require a coplanar arrangement.

The isolation of material containing a 3β-formate function from the acid-catalysed and thermal reactions of (1) points to the involvement of the intramolecular hemiacetal (22) in these reactions as well. With trifluoroacetic acid, the diene (19) ($\lambda_{max.}$ 239 nm) was obtained in an 80% yield. This reaction proceeds *via* the allylic alcohol (16), which would readily undergo dehydration in the presence of acid.[1] When a solution of (1) in xylene was heated at reflux for 11 h, the allylic alcohol (16) was obtained in 77% yield. Oxidation of the 6β-alcohol (16) to the α,β-unsaturated ketone (20) followed by hydrolysis of the formate group afforded the known [11] 3β-alcohol (21).



(23) (24)

SCHEME 2

EXPERIMENTAL

M.p.s were determined with a Hoover Uni-melt apparatus. Optical rotations were obtained with a Perkin-Elmer 141 polarimeter for solutions in chloroform. U.v. spectra were recorded with a Bausch and Lomb Spectronic 600 instrument. ^{1}H N.m.r. spectra were obtained with a Varian T-60 instrument (deuteriochloroform as solvent and tetramethylsilane as internal standard). Mass spectra were obtained with an A.E.I. MS9025 spectrometer. Light petroleum was of boiling range 30—60 °C. The reactions were monitored by t.l.c. using Merck pre-coated silica gel 60 F-254 plates. Microanalyses were carried out by Galbraith Laboratories, Knoxville, TN 37921, U.S.A.

General Procedures.—(i) The oxidation of alcohols to aldehydes or ketones was accomplished with pyridinium chlorochromate in the presence of sodium acetate according to the published procedure.[12]

(ii) Work-up involved pouring the reaction mixture into water, extracting with methylene chloride, and then washing the combined extracts with water. After the extracts were dried (Na_2SO_4), the solvents were removed.

(iii) Chromatography refers to column chromatography employing silica gel (Baker 20—200 mesh) with ethyl acetate–hexane as eluant.

5,6β-Epoxy-3β-hydroxy-5β-cholestan-19-al (1).—Oxidation of 3β-acetoxy-5,6β-epoxy-5β-cholestan-19-ol (3) [13] (1.00 g) afforded, after chromatography, 3β-acetoxy-5,6β-epoxy-5β-cholestan-19-al (2) (820 mg, 82%), m.p. 138—140 °C (needles from methanol) (lit.,[3] 138—140 °C); $\nu_{max.}$ 1 725 cm^{-1} (acetate and CHO); δ 1.95 (s, 3 H, OAc), 3.15 (m, 1 H, $W_{\frac{1}{2}}$ *ca.* 5 Hz, 6α-H), 4.73 (m, 1 H, $W_{\frac{1}{2}}$ *ca.* 22 Hz, 3α-H), 9.77 (s, 1 H, 19-H) (Found: C, 76.05; H, 10.2. $C_{29}H_{46}O_4$ requires C, 75.95; H, 10.1%). Hydrolysis of the acetate (3) (525 mg) with aqueous sodium hydroxide (2 ml; 1.0M) in methanol (50 ml) under nitrogen at room temperature (1 h) afforded, after work-up and chromatography, the alcohol (1) (442 mg, 92%), m.p. 119—132 °C (fine needles from methanol); $[\alpha]_D$ (initial) −39° (*c* 4.5) (after 24 h, −18°) (lit.,[3] m.p. 138—140 °C; $[\alpha]_D$ −10°); $\nu_{max.}$ 3 600, 3 460 (OH), and 1 720 cm^{-1} (CHO) (Found: C, 77.75; H, 10.75. $C_{27}H_{44}O_4$ requires C, 77.85; H, 10.65%).

5,6α-Epoxy-3β-hydroxy-5α-cholestan-19-al (9).—Oxidation of 3β-acetoxy-5,6α-epoxy-5α-cholestan-19-ol (11) [1] (1.00 g) afforded, after chromatography, 3β-acetoxy-5,6α-epoxy-5α-cholestan-19-al (10) (890 mg, 89%), m.p. 132—134 °C (needles from methanol); $\nu_{max.}$ 1 725 cm^{-1} (acetate CO and CHO); δ 1.97 (s, 3 H, OAc), 3.10 (app. d, 1 H, *J ca.* 4 Hz, 6β-H), 4.90 (m, 1 H, $W_{\frac{1}{2}}$ *ca.* 24 Hz, 3α-H), and 9.82 (s, 1 H, 19-H) (Found: C, 76.05; H, 10.05. $C_{29}H_{46}O_4$ requires C, 75.95; H, 10.1%). Hydrolysis of the acetate (10) (430 mg) with aqueous sodium hydroxide (1.5 ml; 1.0M) in methanol (60 ml) under nitrogen at room temperature afforded, after work-up and chromatography, the *alcohol* (9) (352 mg, 90%), m.p. 125—137 °C (plates from methanol); $[\alpha]_D$ (initial) −54° (*c* 5.3) (after 24 h, −46°); $\nu_{max.}$ 3 600, 3 460 (OH), and 1 720 cm^{-1} (CHO); δ (after 18 h) 3.10 (m, 1 H, 6β-H), 4.0 (m, 1 H, $W_{\frac{1}{2}}$ *ca.* 30 Hz, 3α-H), 5.28 (s) and 9.80 (s) (1 H, 1 : 3.5, 19-H); *m/z* 416 (M^+) (Found: C, 76.5; H, 10.9. $C_{27}H_{44}O_3 0.5H_2O$ requires C, 76.15; H, 10.65%).

5,6β-Epoxy-3β-methoxy-5β-cholestan-19-al (4).—A solution of 3β-acetoxy-19-dimethyl(t-butyl)silyloxy-5,6β-epoxy-5β-cholestane (5) [1] (1.40 g) in methanol (25 ml) containing aqueous sodium hydroxide (4.9 ml, 1.0 m) was heated at reflux for 1 h. The crude alcohol (6), obtained after work-up, was dissolved in methylene chloride (20 ml) and an aqueous solution of potassium hydroxide (10 ml; 20%) was added. This mixture was stirred at room temperature and four additions of methyl iodide (0.23 ml, 1.5 equiv.) and benzyl triethylammonium chloride (100 mg) were made over a period of 2 days. Work-up and chromatography afforded *19-dimethyl(t-butyl)silyloxy-5,6β-epoxy-3β-methoxy-5β-cholestane* (7) (736 mg, 65%), m.p. 87—88 °C (needles from acetone–water); $[\alpha]_D$ 0° (*c* 4.5); δ 0.07 (s, Me_2Si), 0.90 (s, Bu^tSi), 2.90 (m, 1 H, $W_{\frac{1}{2}}$ *ca.* 5 Hz, 6α-H), *ca.* 3.2 (m) and 3.30 (s) (4 H, 3α-H and 3β-OMe), 3.70 (s, 2 H, 19-H_2) (Found: C, 74.9; H, 11.55. $C_{34}H_{62}O_3Si$ requires C, 74.65; H, 11.4%), and unchanged (*19-dimethyl(t-butyl)silyloxy-5,6β-epoxy-5β-cholestan-3β-ol* (6) (440 mg, 34%), m.p. 73—76 °C (needles from acetone–water); $[\alpha]_D$ +2° (*c* 8.9); δ 0.08 (s, Me_2Si), 0.90 (s, Bu^tSi), 2.93 (m, 1 H, $W_{\frac{1}{2}}$ *ca.* 5 Hz, 6α-H), and *ca.* 3.7 (m) and 3.72 (s), (3 H, 3α-H and 19-H_2) (Found: C, 74.45; H, 11.5. $C_{33}H_{60}O_3Si$ requires C, 74.4; H, 11.35%). To the methyl ether (7) (700 mg) in tetrahydro-

furan (4 ml) was added a solution of tetrabutylammonium fluoride (2.6 ml, 1M), in tetrahydrofuran. After 3 days, work-up followed by chromatography afforded starting material (7) (98 mg, 14%) and 5,6β-*epoxy*-3β-*methoxy*-5β-*cholestan*-19-*ol* (8) (344 mg, 62%), m.p. 133—134 °C (needles from methanol); $[\alpha]_D$ +17° (*c* 1.5); $\nu_{max.}$ 3 500 cm^{-1} (OH); δ (after D_2O addition) 3.03 (m, 1 H, $W_{\frac{1}{2}}$ *ca.* 5 Hz, 6α-H) *ca.* 3.2 (m) and 3.32 (s) (4 H, 3α-H and 3β-OMe), and 3.87 (q, δ_A 4.17, δ_B 3.57, J_{AB} 12 Hz, 19-H_2) (Found: C, 77.9; H, 11.0. $C_{28}H_{48}O_3$ requires C, 77.7; H, 11.2%). Oxidation of the 19-alcohol (8) (300 mg) afforded, after chromatography, the *aldehyde* (4) (236 mg, 77%), m.p. 102—103 °C (needles from methanol); $[\alpha]_D$ −80° (*c* 1.8); $\nu_{max.}$ 1 720 cm^{-1} (CHO); δ 2.97 (m), *ca.* 3.2 (m), and 3.27 (s) (5 H, 6α-H, 3α-H, and 3β-OMe), and 9.75 (s, 1 H, 19-H) (Found: C, 78.3; H, 19.9. $C_{28}H_{46}O_3$ requires C, 78.1; H, 19.75%).

Reactions of the Epoxy-19-aldehydes (1), (4), *and* (9) *with Base.*—(a) *Aqueous 20% potassium hydroxide.* To a solution of the epoxide (100 mg) in methanol (10 ml) under nitrogen was added aqueous potassium hydroxide (2 ml; 20%) and the mixture was heated at reflux. This was followed by work-up and column chromatography.

The 3β-hydroxy-5β,6β-epoxide (1) afforded (after 36 h reflux), 3β,6β-dihydroxy-19-norcholest-5(10)-ene (14) (73 mg, 78%), m.p. 166—168 °C (needles from methanol); $[\alpha]_D$ +101° (*c* 2.2) (lit.,[3] m.p. 166—168 °C; $[\alpha]_D$ +98°); δ 3.78 (m, 1 H, $W_{\frac{1}{2}}$ *ca.* 7 Hz, 6α-H) and 4.07 (m, 1 H, $W_{\frac{1}{2}}$ *ca.* 12 Hz, 3α-H).

The 3β-methoxy-5β,6β-epoxide (4) afforded (after 108 h reflux) starting material (30 mg, 30%) and 6β-*hydroxy*-3β-*methoxy*-19-*norcholest*-5(10)-*ene* (15) (46 mg, 49%), m.p. 109—111 °C (needles from light petroleum); $[\alpha]_D$ +103° (*c* 0.9); $\nu_{max.}$ 3 600 and 3 420 cm^{-1} (OH); δ 3.33 (s, 3β-OMe), *ca.* 3.5 (m, 3α-H), and 3.78 (m, $W_{\frac{1}{2}}$ *ca.* 8 Hz, 6α-H) (Found: C, 80.85; H, 11.45. $C_{27}H_{46}O_2$ requires C, 80.55; H, 11.5%).

(b) *Methanolic potassium hydroxide.* To a solution of the 3β-hydroxy-5α,6α-epoxide (9) (100 mg) in methanol (10 ml) under nitrogen was added methanolic potassium hydroxide (2 ml; 3.8M) and the mixture was heated at reflux for 1.5 h. Work-up followed by chromatography allowed isolation of the major component (71 mg) contaminated with some unidentified material. Crystallisation from methanol afforded pure 3β,5-*dihydroxy*-6β-*methoxy*-5α-*cholestan*-19-*al* (17), m.p. 197—199°; $[\alpha]_D$ +7° (*c* 1.0); $\nu_{max.}$ (KBr) 3 620, 3 360 (OH), and 1 690 * cm^{-1} (CHO); δ 3.15 (m, 1 H, $W_{\frac{1}{2}}$ *ca.* 5 Hz, 6α-H), 3.32 (s, 3 H, OMe), 3.98 (m, 1 H, $W_{\frac{1}{2}}$ *ca.* 26 Hz, 3α-H), and 10.2 (s, 1 H, CHO) (Found: C, 74.95; H, 10.95. $C_{28}H_{48}O_4$ requires C, 74.95; H, 10.8%). Acetylation (acetic anhydride–pyridine) gave the 3β-acetate (18), $\nu_{max.}$ 3 600, 3 420 (OH), and 1 720 cm^{-1} (acetate CO and CHO); δ 1.97 (s, 3 H, OAc), 3.13 (m, 1 H, $W_{\frac{1}{2}}$ *ca.* 5 Hz, 6α-H), 3.30 (s, 3 H, OMe), 5.11 (m, 1 H, $W_{\frac{1}{2}}$ *ca.* 26 Hz, 3α-H), and 10.2 (s, 1 H, CHO).

(c) *Sodium methoxide.* A solution of the 3β-hydroxy-5β,6β-epoxide (1) (70 mg) in methanol containing sodium methoxide (2 ml; 0.55M) was heated at reflux for 142 h under nitrogen. The mixture was worked up and chromatographed. The first component obtained was (¹H n.m.r.) a mixture of starting material and an unidentified compound. The second component (37 mg, 57%) was the allylic alcohol (14) (t.l.c. and ¹H n.m.r.).

(d) *Magnesium methoxide.* To a solution of the epoxide (70 mg) in methanol (7 ml) under nitrogen was added methanolic magnesium methoxide (2 ml; 0.4M) and the mixture was heated at reflux for the specified period.

The 3β-hydroxy-5β,6β-epoxide (1) afforded (after 20 min reflux) the allylic alcohol (14) (59 mg, 90%) (t.l.c. and ¹H n.m.r.).

The 3β-methoxy-5β,6β-epoxide (4) afforded (after 97 h reflux) starting material (24 mg, 35%) (t.l.c. and ¹H n.m.r.) and the 19-hydroxy-5β,6β-epoxide (8) (37 mg, 56%) (t.l.c. and ¹H n.m.r.).

Acid-catalysed Reaction of 5,6β-*Epoxy*-3β-*hydroxy*-5β-*cholestan*-19-*al* (1).—Trifluoroacetic acid (0.05 ml) was added to a solution of the epoxide (1) (70 mg) in dry methylene chloride under nitrogen. After 15 min, the reaction was stopped by addition of saturated aqueous sodium hydrogen carbonate (5 ml). Work-up followed by column chromatography gave 3β-*formyl*-19-*norcholesta*-1(10),5-*diene* (19) (56 mg, 80%) as a solid, m.p. 67—68°, $\lambda_{max.}$ (ethanol) 239 nm (ε 15 000); $\nu_{max.}$ 1 720 cm^{-1} (OCHO); δ 4.9—5.3 (m, 3 H, 1-H, 3α-H, 3α-H, 6-H) and 7.98 (s, 1 H, OCHO) (Found: C, 81.2; H, 10.75. $C_{27}H_{42}O_3$ requires C, 81.35; H, 10.6%).

Thermal Rearrangement of 5,6β-*Epoxy*-3β-*hydroxy*-5β-*cholestan*-19-*al* (1).—A solution of the epoxide (1) (375 mg) in xylene (10 ml) was heated at reflux for 11 h under nitrogen. Removal of the solvent followed by chromatography afforded 3β-*formyloxy*-6β-*hydroxy*-19-*norcholest*-5(10)-*ene* (16) (287 mg, 77%) as an oil, $[\alpha]_D$ +99° (*c* 4.0); $\nu_{max.}$ 3 605, 3 440 (OH), and 1 715 cm^{-1} (OCHO); δ 3.80 (m, 1 H, $W_{\frac{1}{2}}$ *ca.* 7 Hz, 6α-H), 5.20 (m, 1 H, $W_{\frac{1}{2}}$ *ca.* 13 Hz, 3α-H), and 8.00 (s, 1 H, OCHO) (Found: C, 77.65; H, 10.85. $C_{27}H_{44}O_3$ requires C, 77.85; H, 10.65%).

Hydrolysis of a sample of the 3β-formate (16) (methanol, aqueous M-sodium hydroxide, 1 h) afforded the diol (14) (t.l.c. and ¹H n.m.r.).

Oxidation of the 3β-formate (16) (96 mg) afforded crude 3β-*formyloxy*-19-*norcholest*-5(10)-*en*-6-*one* (20) as an oil, $\nu_{max.}$ 1 720 (OCHO), and 1 660 and 1 625 cm^{-1} (α,β-unsaturated ketone); δ 5.30 (m, 1 H, $W_{\frac{1}{2}}$ *ca.* 13 Hz, 3α-H) and 8.07 (s, 1 H, OCHO). This was taken up in methanol (4 ml) and treated with aqueous sodium hydroxide (1 ml; 1.0M). After 1 h, the mixture was worked up and chromatographed to give 3β-*hydroxy*-19-*norcholest*-5(10)-*en*-6-*one* (21) (39 mg, 43%), m.p. 145—146 °C (plates from methanol–water) (lit.,[11] 147—148 °C); $\nu_{max.}$ 3 620 and 3 460 (OH), and 1 660 and 1 625 cm^{-1} (α,β-unsaturated ketone); δ 4.07 (m, $W_{\frac{1}{2}}$ *ca.* 14 Hz, 3α-H).

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* The unusually low frequency for the aldehyde absorption suggests either an intermolecular or an intramolecular hydrogen bond [14] in the crystalline state.

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