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REACTIONS OF EPOXIDES—XXIV*

THE BF_3-CATALYSED REARRANGEMENT OF 4,5- AND 5,6-EPOXYCHOLESTANES

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Abstract—4α,5α, 4β,5β- and 5β,6β-Epoxycholestanes give backbone rearranged compounds on BF_3-catalysed rearrangement. Solvent changes markedly affect the products of rearrangement. 4α-Hydroxy-compounds arise from the 4β,5β-epoxide on BF_3-catalysed rearrangement.

DURING studies directed towards the determination of the kinetic isotope effect for the BF_3-catalysed conversion of an epoxide into a ketone involving a 1,2-hydride shift (Fig. 1) we required a steroid epoxide which rearranges in high yield to a ketone.

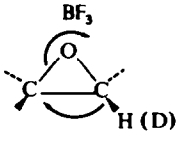

FIG. 1

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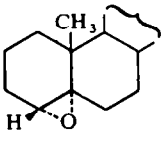

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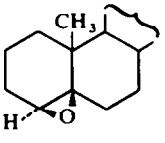

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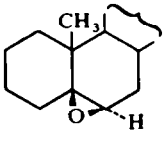

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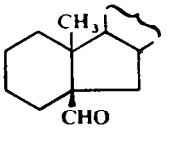

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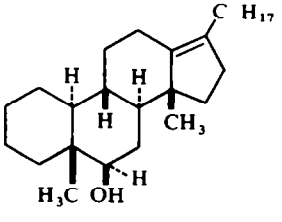

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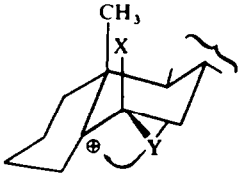
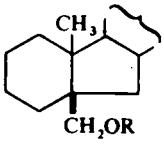
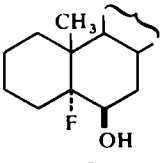


6: X = $OBF_3^{\ominus}$, Y = H for β-epoxide
X = H, Y = $OBF_3^{\ominus}$ for α-epoxide



7[A]: R = H
[B]: R = Ts



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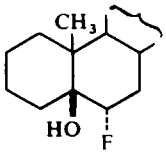

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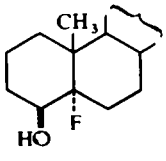

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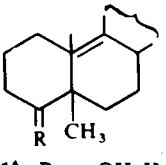

11[A]: R = αOH, H
[B]: R = O

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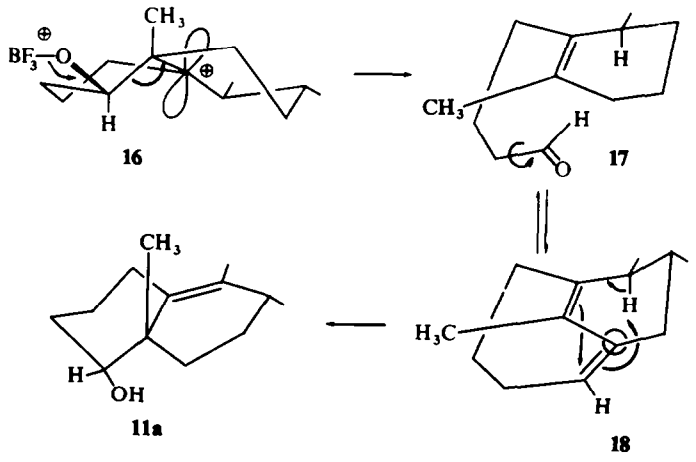
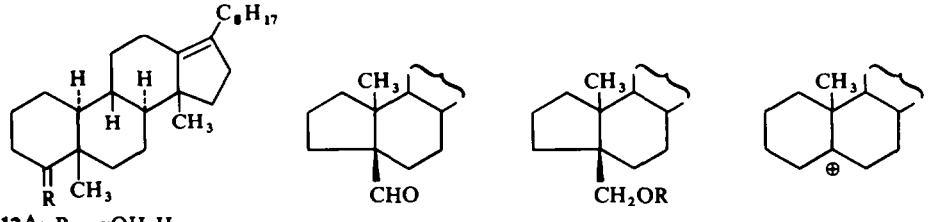


FIG. 2



The rearrangements of 4α,5α-epoxy-[1,2] (1), 4β,5β-epoxy-[1] (2) and 5β,6β-epoxy-[2] (3) cholestanes with $BF_3 \cdot Et_2O$ in benzene have been reported to give crude products from which the corresponding ketones could be crystallized. As a preliminary to the kinetic isotope study we examined the $BF_3 \cdot Et_2O$ catalysed reactions of these epoxides in benzene, benzene–ether, and ether solution. The results of these experiments were significantly at variance with the earlier reports and are given below. The 4β,5β- (2) and 5β,6β- (3) epoxides were prepared by treatment of the 4β,5α-diacetate[1] and the 5α,6β-diacetate[3] with KOH–ethanol.

Rearrangements of 5,6β-*epoxy*-5β-*cholestane* (3). Reaction of the epoxide (3) with $BF_3 \cdot Et_2O$ in benzene was rapid (2 min, TLC). Chromatography on alumina allowed the separation of the products, cholesta-3,5-diene (15%; possibly containing some cholesta-4,6-diene), 5-formyl-B-nor cholestane (4; 18%), cholestan-6-one (20%) and the 6β-hydroxy-$\Delta^{13(17)}$-compound (5; 46%). The aldehyde (4) is identical with the aldehyde product from the rearrangement of 5,6α-epoxy-5α-cholestane.[4,*] On mechanistic grounds it seems more probable that the aldehyde (4) has the 5β-configuration, and that it is formed by rearrangement of the C-5 carbonium ion in conformation (6). In an attempt to establish the C-5 stereochemistry, the aldehyde

* It seems probable that the more flexible ring A would accommodate the conformational changes involved in introducing an sp^2 centre at C-5.

(4) was reduced by LAH to the alcohol (**7a**), the tosylate (**7b**) of which surprisingly gave cholest-4-ene on treatment with LAH. An analogous reaction involving an A-nor-system is reported below.

The structure of the 6β-hydroxy-$\Delta^{13(17)}$-compound (**5**) followed from a consideration[5] of its UV and NMR spectra (Experimental).

Reaction of the 5β,6β-epoxide (**3**) with $BF_3 \cdot Et_2O$ in Et_2O solution was slow (2½ hr; TLC). The products, separated by alumina chromatography, were a fluorine containing compound ($C_{27}H_{47}OF$, mass spectrum; 6%), a mixture of $\Delta^{3,5}$- and $\Delta^{4,6}$-cholestadienes (22%), the fluorohydrin (**8**; 57%), and the $\Delta^{13(17)}$-compound (**5**; 9%). The fluorine containing compound produced in low yield is tentatively assigned the 6α-fluoro-5β-hydroxy-structure (**9**).

In order to investigate the possibility of fluorohydrin (**8**) intermediacy in the formation of rearrangement products from the $BF_3 \cdot Et_2O$–benzene reaction, the fluorohydrin (**8**) was treated with $BF_3 \cdot Et_2O$–benzene. The reaction, followed[6] by TLC, was rapid (20 sec). The products formed were those isolated from the epoxide–$BF_3 \cdot Et_2O$–benzene reaction, but with a significant increase in the yield of the 6β-hydroxy-$\Delta^{13(17)}$-olefin (**5**).

Rearrangements of 4α,5-*epoxy*-5α-*cholestane* (**1**). Reaction of the epoxide (**1**) with $BF_3 \cdot Et_2O$–benzene (45 sec) gave unidentified non-polar material (6%), 5β-cholestan-4-one (76%), and the 4α-hydroxy-$\Delta^{13(17)}$-compound (**12a**; 11%). The $\Delta^{13(17)}$-compound (**12a**) was identified by means of its UV and NMR spectra,[5] and its conversion on oxidation into the known[7] 4-ketone (**12c**).

In contrast reaction with $BF_3 \cdot Et_2O$ was slower; after 15 hr starting material (28%) was isolated. In addition to a reduced yield of 5β-cholestan-4-one (20%) were isolated a mixture of $\Delta^{3,5}$- and $\Delta^{4,6}$-cholestadienes (14%), cholest-5-en-4α-ol (14%) and two other unidentified polar compounds (total 9%).

Rearrangements of 4β-5-*epoxy*-5β-*cholestane* (**2**). Brief reaction of epoxide (**2**) with $BF_3 \cdot Et_2O$ in benzene gave a mixture of $\Delta^{3,5}$- and $\Delta^{4,6}$-cholestadienes (8%), 5α-cholestan-4-one (41%), the fluorohydrin (**10**; 3%), the 4α-hydroxy-Δ^{9}-compound (**11a**: 11%), the 4β-hydroxy-$\Delta^{13(17)}$-compound (**12b**; 23%), the 4α-hydroxy-$\Delta^{13(17)}$-compound (**12a**; 3%), and the 5β-formyl-A-nor cholestane (**13**; 7%). The identity of the unexpected 4α-hydroxy-Δ^{9}-compound (**11a**) was established by a consideration of its UV and NMR spectra, and by its conversion on oxidation with CrO_3–pyridine into the known[7] unsaturated ketone (**11b**). The 5-formyl compound (**13**) is tentatively assigned the 5β-configuration. Reduction of the aldehyde (**13**) gave the alcohol (**14a**), the tosylate (**14b**) of which gave cholest-4-ene on reaction with LAH. The reactions of tosylate (**7b** and **14b**) with LAH are regarded as proceeding *via* heterolysis of the tosylate with nor-ring expansion to give the C-5 carbonium ion (**15**) which suffers removal of the more accessible 4β-proton to give cholest-4-ene.

Reaction of epoxide (**2**) with $BF_3 \cdot Et_2O$ in Et_2O gave the fluorohydrin (**10**; 67%) as the major product accompanied by cholesta-3,5-diene (6%), 5α-cholestan-4-one (6%) and a mixture of two unidentified polar compounds (9%).

Reaction of the fluorohydrin (**10**) with $BF_3 \cdot Et_2O$ in benzene was rapid (10 sec). Apart from unidentified non-polar material (8%), the reaction products were 5α-cholestan-4-one (28%) and the 4β-hydroxy-$\Delta^{13(17)}$-compound (**12b**; 56%). The significantly higher yield of the 4β-hydroxy-$\Delta^{13(17)}$-compound (**12b**) from the fluorohydrin reaction (compared with the epoxide reaction) may be rationalised in terms

of a BF_3-catalysed heterolysis of the C^5-F bond, without involvement of the 4β-OH group, leading directly to backbone rearrangement.

DISCUSSION

For the 4β,5β-epoxide (**2**) and the 5β,6β-epoxide (**3**) rearrangements the nature of the products of BF_3-catalysed rearrangement are markedly dependent on the solvent used, ether or benzene. Furthermore the rate of product formation is notably greater in benzene. For reactions of the 4β,5β-epoxide (**2**) in benzene–Et_2O solvent systems the products were those of the 'Et_2O reaction' on admixture of only 4% Et_2O to the reaction solvent. Even for the benzene −1% Et_2O solvent system the fluorohydrin (**10**) was a significant product from the $BF_3 \cdot Et_2O$ catalysed reaction.

The isolation of the 4α-hydroxy-Δ^9- (**11a**) and 4α-hydroxy-$\Delta^{13(17)}$- (**12a**) compounds from the rearrangement of the 4β,5β-epoxide (**2**) was unexpected. These compounds are considered to arise by the mechanistic route shown in (Fig. 2). Cleavage of the $C_{5\beta}$-O bond followed by migration of the 19-Me group to the 5β-position gives the C-10 carbonium ion (**16**). From the C-10 carbonium ion (**16**) the normal sequence of 1,2-hydride and 1,2-Me shifts would lead to the expected (and found) 4β-hydroxy-$\Delta^{13(17)}$-compound (**12b**). However, the preferred conformation of **16** allows a fragmentation reaction[8] to give the A-seco-5-methyl-$\Delta^{5(10)}$-4-aldehyde (**17**). Reversal of this process in conformation **17** leads back to the C-10 carbonium ion (**16**), and ultimately to the 4β-hydroxy-$\Delta^{13(17)}$-compound (**12b**). For the A-seco-aldehyde in conformation **18** cyclization may occur *via* a cyclic transition state[9] with 9α-H removal by the aldehyde oxygen atom and leading directly to the 4α-hydroxy-Δ^9-compound (**11a**). The origin of the 4α-hydroxy-$\Delta^{13(17)}$-compound (**12a**) is not clear. It may arise by simple $\Delta^9 \rightarrow \Delta^{13(17)}$-olefin isomerization or it may represent the component of '4α-OH cyclization' where 9α-proton removal is not effected by the aldehyde O atom.

EXPERIMENTAL

Rotations were measured for $CHCl_3$ solns at room temp. IR spectra were recorded on a Perkin Elmer 337 spectrometer. UV spectra were recorded for cyclohexane solns. Alumina used for chromatography was P. Spence, Grade H, deactivated by the addition of 5% of 10% AcOH. Silica gel used for chromatography was Crosfield Sorbsil Grade 60–120. Light petroleum refers to the fraction b.p. 50–70°. NMR spectra were determined at 60 Mc in $CDCl_3$ with $CHCl_3$ and TMS as internal standards.

4β,5-*Epoxy*-5β-*cholestane* (**2**). The epoxide prepared by the method of Shoppee *et al.*,[1] m.p. 64–65°, $[\alpha]_D$ +6° (Lit. values:[1] m.p. 60–62°, $[\alpha]_D$ +3·5°), NMR 2·88 ppm (4α-H); 1·01 ppm ($C^{19}H_3$); 0·67 ppm ($C^{18}H_3$).

5,6β-*Epoxy*-5β-*cholestane* (**3**). The epoxide prepared by the method of Hallsworth and Henbest,[3] m.p. 79–80°, $[\alpha]_D$ +6° (*c* 1·00) (Lit. values:[3] m.p. 80–81°, $[\alpha]_D$ +8°); NMR 2·99 ppm (6α-H); 0·98 ppm ($C^{19}H_3$); 0·65 ppm ($C^{18}H_3$).

Rearrangements of 5,6β-*epoxy*-5β-*cholestane* (**3**).

(a) *in benzene.* The epoxide (498 mg) in benzene (70 ml) was treated with $BF_3 \cdot Et_2O$ (0·5 ml) and kept at 20° for 2 min. The reaction was quenched with Na_2CO_3 aq and the crude product, isolated by means of Et_2O, adsorbed onto alumina (50 g). Elution with light petroleum gave cholesta-3,5-diene, contaminated with cholesta-4,6-diene, (77 mg), m.p. 78–79°, $[\alpha]_D$ −79° (*c* 1·01). The major component was identified by comparison of NMR spectra with authentic material. Continued elution with light petroleum gave **4** (87 mg) as a gum, ν_{max} (Nujol) 2720, 1728 cm^{-1}; NMR 9·78 ppm (CHO; singlet); 0·88 ppm ($C^{19}H_3$); 0·66 ppm ($C^{18}H_3$); identical in all respects with the aldehyde[4] from 5,6α-epoxy-5α-cholestane. The aldehyde rapidly decomposed on storage.

Elution with light petroleum–benzene (20:1) gave 5α-cholestan-6-one (100 mg) as prisms, m.p. 99·5–100·5°, $[\alpha]_D$ +1° (*c* 1·01), ν_{max} (Nujol) 1715 cm^{-1}; NMR 0·73 ppm ($C^{19}H_3$); 0·68 ppm ($C^{18}H_3$); (Lit. values[10]: m.p. 98°; $[\alpha]_D$ −7°).

Finally elution with benzene gave the 6β-*hydroxy*-$\Delta^{13(17)}$-compound (225 mg; **5**) m.p. 92–94°, $[\alpha]_D$ +20° (*c* 1·05), ν_{max} 3340 cm^{-1}, ε 201 nm 9400; NMR 3·27 ppm ($W_{h/2}$ 18 c/s; 6α-H); 0·95 ppm (*J* = 6 c/s; $C^{21}H_3$; decoupled with −88 c/s) 0·92 ppm (14β-Me); 0·84 ppm (5β-Me), (Found: C, 84·1; H, 12·2. $C_{27}H_{46}O$ requires, C, 84·0; H, 11·9%).

(b) *In* Et_2O. The epoxide (387 mg) in Et_2O (60 ml) was treated with $BF_3 \cdot Et_2O$ (1 ml) and kept at 20° for 2½ hr. The reaction was quenched with Na_2CO_3 aq and the crude product, isolated by means of Et_2O, adsorbed onto alumina (50 g).

Elution with light petroleum gave a solid (107 mg), which on crystallization from light petroleum–acetone gave needles (23 mg; **9**), m.p. 227° (dec), (M^+ 406·3614; calculated for $C_{27}H_{47}FO$, 406·3611). The residue (85 mg) was shown (TLC, NMR) to consist of a mixture of cholesta-3,5-diene and cholesta-4,6-diene.

Elution with light petroleum–benzene (4:1) gave 5α-*fluoro*-6β-*hydroxycholestane* (220 mg; **8**) as a gum, $[\alpha]_D$ +4° (*c* 0·98), ν_{max} (CCl_4) 3625 cm^{-1}; NMR 3·69 ppm ($W_{h/2}$ 11 c/s; 6α-H), 1·11 ppm ($C^{19}H_3$); 0·68 ppm ($C^{18}H_3$) (Found: C, 80·2; H, 11·8. $C_{27}H_{47}FO$ requires: C, 79·8; H, 11·6%).

Elution with benzene–Et_2O (10:1) gave the 6β-hydroxy-$\Delta^{13(17)}$-compound (36 mg; **5**), identified by comparison (IR, NMR and TLC) with authentic material.

BF_3-*Catalysed reaction of fluorohydrin* (**8**).

The fluorohydrin (5 mg) in benzene (0·5 ml) was treated with $BF_3 \cdot Et_2O$ (5μl), and the reaction followed by TLC. The reaction was complete in 20 sec. The products were the same as those for the epoxide $BF_3 \cdot Et_2O$-benzene reaction, except that the 6β-hydroxy-$\Delta^{13(17)}$-compound was found in higher yield.

Rearrangements of 4α,5-*epoxy*-5α-*cholestane* (**1**).

(a) *In benzene.* The epoxide (420 mg) in benzene (40 ml) was treated with $BF_3 \cdot Et_2O$ (0·7 ml). After 45 sec at 20° the reaction was quenched with Na_2CO_3 aq and the crude product, isolated by means of Et_2O, was adsorbed onto alumina (30 g). Elution with pentane gave a non-polar compound (25 mg) followed by 5β-cholestan-4-one (320 mg) as needles (MeOH), m.p. 108·5–109·5°, $[\alpha]_D$ +41° (*c* 1·02), ν_{max} (Nujol) 1705 cm^{-1} (Lit. values[1]: m.p. 109°, $[\alpha]_D$ +40°; NMR 1·11 ppm ($C^{19}H_3$), 0·64 ppm ($C^{18}H_3$).

Elution with benzene gave **12a** (44 mg) as a gum, $[\alpha]_D$ −1° (*c* 0·98), ν_{max} (Nujol) 3400 cm^{-1}, 197 nm 9500; NMR 3·31 ppm ($W_{h/2}$ 6 c/s; 4β-H); 0·95 ppm (*J* = 6 c/s, decoupled-88 c/s; $C^{21}H_3$); 0·90 ppm (14β-Me); 0·86 ppm (5β-Me).

(b) *In* Et_2O. The epoxide (137 mg) in Et_2O (25 ml) was treated with $BF_3 \cdot Et_2O$ (0·15 ml) and kept at 20° for 15 hr. The reaction was quenched with Na_2CO_3 aq and the crude product, isolated by means of Et_2O, adsorbed onto alumina (20 g). Elution with light petroleum gave a mixture of two compounds (12 mg), ν_{max}, (CCl_4) 3635 cm^{-1} which were not identified. Elution with benzene and crystallization from MeOH gave 4α-hydroxycholest-5-ene (20 mg), m.p. and m.m.p. 140–141°, $[\alpha]_D$ −38° (*c* 0·99) (Lit. values[11]: m.p. 144–145°, $[\alpha]_D$ −50°); NMR 5·66 ppm ($W_{h/2}$ 11 c/s; 6-H); 4·20 ppm ($W_{h\cdot2}$ 18 c/s; 4β-H); 0·99 ppm ($C^{19}H_3$); 0·68 ppm ($C^{18}H_3$).

Rearrangements of 4β,5-*epoxy*-5β-*cholestane* (**2**)

(a) *In benzene.* The epoxide (361 mg) in benzene (40 ml) was treated with $BF_3 \cdot Et_2O$ (0·4 ml) and kept at 20° for 2 min. The reaction was quenched with Na_2CO_3 aq and the crude product, isolated by means of Et_2O, adsorbed onto silica (50 g). Elution with light petroleum gave a mixture (30 mg) of cholesta-3,5-diene and cholesta-4,6-diene (TLC, NMR). Further elution with light petroleum the unstable **13** (24 mg), m.p. 58–61° (dec), $[\alpha]_D$ +36° (dec), $[\alpha]_D$ +36° (*c* 1·01), ν_{max} (Nujol) 2720, 1725 cm^{-1}; NMR 9·69 ppm (singlet; CHO); 0·97 ppm ($C^{19}H_3$); 0·67 ppm ($C^{18}H_3$).

Elution with light petroleum–benzene (10:1) and crystallization from acetone gave the 4α-*hydroxy*-Δ^9-*compound* (40 mg; **11a**), m.p. 82–83°, $[\alpha]_D$ +43° (*c* 1·01), ν_{max} (CCl_4) 3640, 3600 cm^{-1}, ε 205 nm 11,300; NMR 3·45 ppm ($W_{h/2}$ 6 c/s; 4β-H); 1·08 ppm (5β-Me); 0·80 ppm ($C^{18}H_3$). (Found: C, 80·4; H, 11·9. $C_{27}H_{46}O \cdot H_2O$ requires: C, 80·1; H, 11·9%).

Further elution with light petroleum–benzene (5:1) gave a mixture of three compounds. This material was adsorbed onto alumina (20 g). Light petroleum–benzene (20:1) eluted cholestan-4-one (147 mg) as needles (MeOH), m.p. and m.m.p. 100–100·5°, $[\alpha]_D$ +31° (*c* 1·05) (Lit. values[12]: m.p. 99–100°, $[\alpha]_D$ +30°).

Elution with benzene gave a mixture (22 mg; ca. 1:1) of **12a** and **10**, identified by comparison (TLC and NMR) with authentic samples.

Elution with light petroleum–benzene (2:1) from the silica column gave the 4β-*hydroxy*-$\Delta^{13(17)}$-*compound* (81 mg; **12b**) as a gum, $[\alpha]_D$ +27° (*c* 0·95); NMR 3·18 ppm ($W_{h/2}$ 19 c/s; 4α-H); 0·95 ppm (*J* 6 c/s, decoupled −88 c/s; $C^{21}H_3$); 0·90 ppm (14β-Me); 0·83 ppm (5β-Me), (Found: C, 80·0; H, 11·9. $C_{27}H_{46}O \cdot H_2O$ requires: C, 80·1; H, 11·9%).

(b) *In* Et_2O. The epoxide (240 mg) in Et_2O (20 ml) was treated with $BF_3 \cdot Et_2O$ (0·35 ml) and kept at 20° for 2 hr. The reaction was quenched with Na_2CO_3 aq and the crude product, isolated by means of Et_2O, adsorbed onto alumina (20 g). Elution with light petroleum gave a mixture of non-polar compounds (28 mg), containing cholesta-3,5-diene (ca. 50%) by NMR and UV. Continued elution with light petroleum gave 5α-cholestan-4-one (15 mg), m.p. and m.m.p. 100–100·5°, ν_{max} (Nujol) 1710 cm^{-1}.

Elution with light petroleum–benzene (20:1) gave the *fluorohydrin* (163 mg; **10**) as needles (MeOH), m.p. 136–137°, $[\alpha]_D$ +18° (*c* 0·95), ν_{max} (Nujol) 3580 cm^{-1}. (Found: C, 80·2; H, 12·0; F, 5·0. $C_{27}H_{47}FO$ requires: C, 79·8; H, 11·6; F, 4·7%); NMR 3·69 ppm ($W_{h/2}$ 12 c/s; 4α-H); 1·14 ppm ($C^{19}H_3$); 0·67 ppm ($C^{18}H_3$).

Elution with light petroleum–benzene (3:2) gave a mixture of two compounds (22 mg) which were not identified.

Rearrangement of fluorohydrin (**10**) *with* $BF_3 \cdot Et_2O$ *in benzene*

The fluorohydrin (39 mg) in benzene (5 ml) was treated with $BF_3 \cdot Et_2O$ (0·2 ml) and kept at 20° for 4 min. The reaction was complete (TLC) in 10 sec. The reaction mixture was quenched with Na_2CO_3 aq and the crude product, isolated by means of Et_2O, was adsorbed onto alumina (9 g). Elution with light petroleum gave two non-polar compounds (3 mg) followed by 5α-cholestan-4-one (11 mg), m.p. and m.m.p. 99·5–100·5°.

Elution with benzene gave the 4β-hydroxy-$\Delta^{13(17)}$-compound (22 mg) identified by comparison (NMR, TLC) with an authentic sample.

Reactions of the 4α-*hydroxy*-Δ^9-*compound* (**11a**)

(a) *Oxidation with* CrO_3-*pyridine*. The alcohol (50 mg) in pyridine (0·5 ml) was treated with CrO_3-pyridine (50 mg in 1·5 ml) and kept at 20° for 12 hr. The product, isolated by means of pentane, was a gum, $[\alpha]_D$ +35° (*c* 0·67), ν_{max} (CCl_4) 1710 cm^{-1}, identical (NMR, TLC) with an authentic sample.[7]

(b) *Acetylation*. The alcohol (80 mg) was treated with Ac_2O (0·3 ml) in pyridine (2 ml) and heated at 100° for 3 hr. Isolation in the usual manner gave the acetate as a gum, ν_{max} 1745, 1245 cm^{-1}; NMR 4·74 ppm ($W_{h/2}$ 6 c/s; 4β-H); 1·09 ppm (5β-Me); 0·79 ppm ($C^{18}H_3$).

(c) *Reaction with* $BF_3 \cdot Et_2O$ *in benzene*. The alcohol (95 mg) in benzene (5 ml) was treated with $BF_3 \cdot Et_2O$ (0·1 ml) and kept at 20° for 75 min. The crude product, isolated in the usual manner, was adsorbed onto alumina (10 g). Elution with light petroleum gave hydrocarbons (8 mg). Elution with light petroleum–benzene (7:1) gave starting material (52 mg). Elution with benzene gave a mixture (20 mg; ca. 1:1) **12a** and **12b**. These materials were identified by comparison (NMR, TLC) with authentic samples.

Reactions of 5β-*formyl-A-norcholestane* (**13**)

Reduction of **13** (154 mg) with LAH in the usual manner gave **14a** (130 mg) as a gum, NMR 3·38 ppm (2H singlet); 0.82 ppm ($C^{13}H_3$); 0·67 ppm ($C^{18}H_3$).

Reaction of **14a** (120 mg) with toluenesulphonyl chloride (120 mg) in pyridine (2 ml) for 3 days at 20°, gave **14b** (120 mg); NMR 3·74, 3·86 ppm (2H); 0·75 ppm ($C^{19}H_3$); 0·63 ppm ($C^{18}H_3$).

Reaction of **14b** (80 mg) with LAH (150 mg) in THF (3 ml) at reflux for 12 hr gave on isolation of the crude product and chromatography on alumina a non-polar material (38 mg). Crystallization from MeOH–Et_2O gave cholest-4-ene (19 mg), identified by comparison with an authentic sample.

Reactions of 5β-*formyl-B-norcholestane* (**4**)

Reduction of **4** (155 mg) as above gave **7a** (150 mg); NMR 3·50, 3·66 ppm (2H); 0·75 ppm ($C^{19}H_3$); 0·63 ppm ($C^{18}H_3$). The alcohol **7a** (145 mg) gave **7b** (125 mg); NMR 3·90, 4·06 ppm (2H); 0·68 ppm ($C^{19}H_3$); 0·61 ppm ($C^{18}H_3$). Reduction of the tosylate (115 mg) with LAH (as above) gave after chromatography on alumina, cholest-4-ene (40 mg) and **7a** (15 mg).

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