Steroids. Part XVII.[1] Functionalisation of the 5β-Methyl Group in 9,10-Epoxy-5-methyl-19-nor-5β-steroids and 5-Methyl-18,19-bisnor-$\Delta^{13(17)}$-5β,8α,9β,10α,14β-steroids

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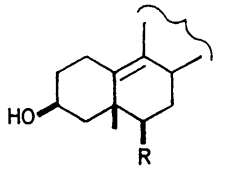
The functionalisation of the 5β-methyl group in the 3β-hydroxy-derivatives of the title compounds is achieved by their reaction with lead tetra-acetate or by photolysis of their nitrite esters. The yields are higher than those previously reported for the related 5-methyl-19-nor-Δ^9-compounds.

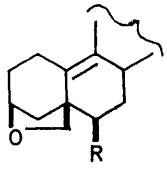
WE have previously reported [2] that compounds of the general type (1) react with lead tetra-acetate in cyclohexane–benzene to give ethers of the type (2). However, in the Barton and hypoiodite reactions,[3] low yields of compounds containing a functionalised 5β-methyl group were obtained. We now report that the 9,10-epoxides (3) and (4) give improved yields of such compounds in the lead tetra-acetate and Barton reactions. In addition, the $\Delta^{13(17)}$-compound (9) is converted cleanly into the ether (13) by its reaction with lead tetra-acetate. These results support our previous suggestion that the 9,10-double bond in (1) causes diversification of the reaction path, particularly in those reactions in which the homoallylic radical (14) is an intermediate.

The 3β-hydroxy-9α,10α-epoxide (3) and the 3β-hydroxy-9β,10β-epoxide (4) were obtained by hydrogenolysis of the corresponding 3β-benzyloxy-compounds (5) and (6).[4] Reaction of the 3β-hydroxy-9,10-epoxides (3) and (4) with lead tetra-acetate gave the ethers (11) (76%) and (12) (50%), respectively. The ^{1}H n.m.r. spectra of the ethers (11) and (12) showed characteristic quartets (τ *ca.* 6·3, J *ca.* 8 Hz) for the 5β-methylene groups.[2]

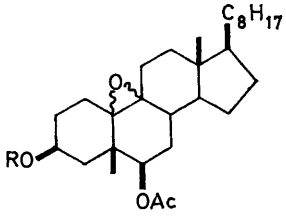
Photolysis of the nitrite esters (7) and (8) in dry benzene gave mixtures which were separated by t.l.c. The 3-ketone (15) (17%), the ether (11) (2·2%), the 3β-hydroxy-5-hydroxymethyl nitrate (17) (6·4%), the 3-alcohol (3) (15%), and the isomeric oximes (19) (4·3%) and (20) (11%) were obtained from the nitrite ester (7). It is likely that the 3-ketone (15) ($\nu_{max.}$ 1720 and 1740 cm^{-1}) and the 3-alcohol (3) arise directly from the thermal decomposition of the nitrite (7), which is known to be catalysed by traces of acid or water.[5] Abstraction of a hydrogen radical from the originally formed 3-alkoxy-radical, in a manner similar to that occurring in the lead tetra-acetate reactions, could account for the small yield of the ether (11). The structure of the 3β-hydroxymethyl nitrate (17) is assigned from spectroscopic data. The i.r. spectrum showed characteristic



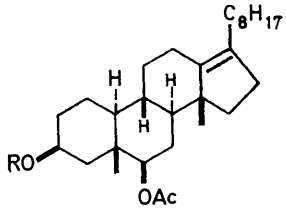
(1)



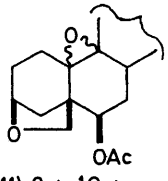
(2)



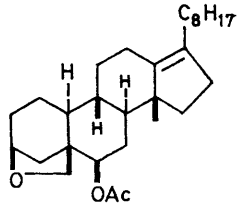
(3) 9α,10α; R = H
(4) 9β,10β; R = H
(5) 9α, 10α; R = PhCH$_2$
(6) 9β, 10β; R = PhCH$_2$
(7) 9α, 10α; R = NO
(8) 9β, 10β; R = NO



(9) R = H
(10) R = PhCH$_2$



(11) 9α, 10α
(12) 9β, 10β



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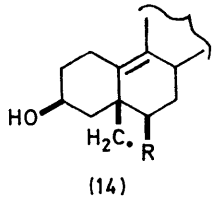
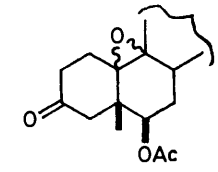


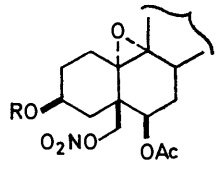
(14)

[1] Part XVI, I. G. Guest and B. A. Marples, *J.C.S. Perkin I*, 1973, 900.
[2] I. G. Guest, J. G. Ll. Jones, B. A. Marples, and M. J. Harrington, *J. Chem. Soc.* (*C*), 1969, 2360.
[3] (*a*) K. Heusler and J. Kalvoda, *Angew. Chem. Internat. Edn.*, 1964, **3**, 525; (*b*) T. B. Windholz and M. Windholz, *ibid.*, 1964, **3**, 353.
[4] J. G. Ll. Jones and B. A. Marples, *J.C.S. Perkin I*, 1972, 792.
[5] D. H. R. Barton, G. C. Ramsay, and D. Wege, *J. Chem. Soc.* (*C*), 1967, 1915.

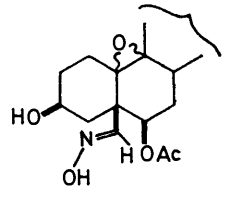
bands at 1645 and 1287 (ONO_2), 1750 ($MeCO_2$), and 3650 (OH) cm^{-1}. The ^1H n.m.r. spectrum showed the 5β-methylene group as a low-field AB quartet (τ 4·95, *J ca.* 12 Hz) [6] and characteristic signals for H-3 (τ 5·75, m, $W_{\frac{1}{2}}$ *ca.* 10 Hz) and H-6 (τ 5·05, t, $W_{\frac{1}{2}}$ *ca.* 20 Hz). Acetylation of the 3β-hydroxy-5-hydroxymethyl nitrate (17) gave the diacetate (18), whose mass spectrum showed no molecular ion but important peaks at *m/e* 517 ($M - NO_2$), 457 (M — AcOH — NO_2), 397 (M — 2AcOH — NO_2), and 367 (M — 2AcOH — NO_2 — CH_2O) in accord with the proposed structure. The 3β-hydroxy-5β-hydroxymethyl nitrate (17) is presumably derived



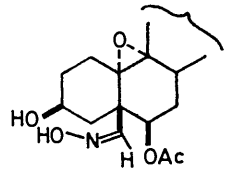
(15) 9α, 10α
(16) 9β, 10β



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



(19) 9α, 10α
(21) 9β, 10β

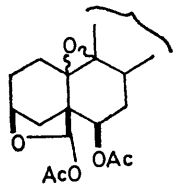


(20)

from the reaction of the intermediate 5β-nitrosomethyl compound with nitric oxide which is present in the solution.[7]

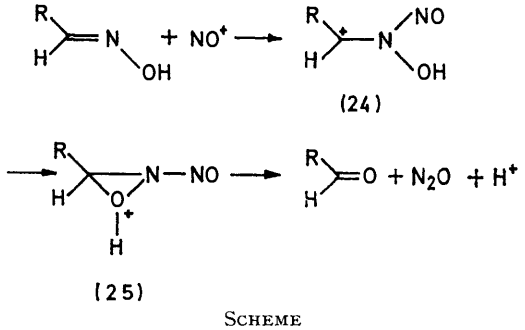
The oximes (19) and (20) were readily identified from their ^1H n.m.r. spectra, which showed singlets for the formyl protons at τ 2·35 and 2·8, respectively. The *E*-configuration was assigned to the compound (19), showing the lower field signal in accord with literature ^1H n.m.r. data for aldoximes.[8]

The 3-ketone (16) (10%), the 3-alcohol (4) (18%), and the oxime (21) (10%) were similarly obtained from the photolysis of the nitrite ester (8). The oxime (21) showed a singlet for the formyl proton at τ 2·5 in the ^1H n.m.r. spectrum, and this does not allow an unequivocal *E*- or *Z*-assignment (however, see below). Treatment of the oximes (19) and (21) with nitrous acid in acetic acid gave the hemiacetal acetates (22) and (23), respectively, which exhibited characteristic singlets for the formyl protons at τ 3·88 and 3·78 respectively in the ^1H n.m.r. spectra.[9] Curiously, the *Z*-oxime (20) did not react with nitrous acid, and it seems likely therefore that the oxime (21) has the *E*-configuration. Wieland and Grimm have shown [10] that nitrous acid deoximation



(22) 9α, 10α
(23) 9β, 10β

involves the formation of the intermediate (25) by intramolecular attack of the oxime hydroxy-group in the carbonium ion (24) (Scheme). A bulky group R in the



(24)

(25)

SCHEME

carbonium ion (24) could seriously influence this reaction in the *Z*-oximes, provided the original configuration of the oxime is at least partially retained in the transition state, and could account for the lack of reactivity of the *Z*-oxime (20).

The 3β-hydroxy-$\Delta^{13(17)}$-compound (9) was obtained by hydrogenolysis of the benzylated compound (10).[4] Reaction of compound (9) with lead tetra-acetate in the usual manner gave ether (13) (56%). The 5β-methylene group in the ether (13) appeared as a triplet (τ 6·3, *J ca.* 8 Hz) in the ^1H n.m.r. spectrum owing to the very similar chemical shifts of the two protons.

Although the yields of oximes in the Barton reactions are low, they represent a considerable improvement over those obtained in the reaction of the Δ^9-compound (1).[2] The homoallylic radical (14) is no longer an intermediate and thus the diversification of the reaction is considerably reduced. The lead tetra-acetate reactions of the 9,10-epoxides and the $\Delta^{13(17)}$-compound (9) are noticeably cleaner than those with the Δ^9-compounds (1) since participation of the double bond in the way previously reported [2] is excluded.

EXPERIMENTAL

Solutions were dried over anhydrous sodium sulphate and solvents were removed *in vacuo* on a rotary evaporator. Plates (1 m × 0·5 mm thick) of Kieselgel PF_{254} (Merck)

[6] B. P. Dailey, A. Gawer, and W. C. Neikam, *Discuss. Faraday Soc.*, 1962, **34**, 18.
[7] O. P. Strausz and H. E. Gunning, *Canad. J. Chem.*, 1963, **41**, 1207.
[8] L. M. Jackman and S. Sternhell, ' Nuclear Magnetic Resonance in Organic Chemistry,' Pergamon, Oxford, 1969, p. 226.
[9] (*a*) C. W. Shoppee, N. W. Hughes, and R. E. Lack, *J. Chem. Soc.* (*C*), 1966, 2359; (*b*) W. Mehrof, K. Irmscher, R. Erb, and L. Pohl, *Chem. Ber.*, 1969, **102**, 643.
[10] T. Wieland and D. Grimm, *Chem. Ber.*, 1963, **96**, 275

were used for preparative t.l.c. I.r. spectra were determined (for solutions in CCl_4 unless specified otherwise) with Perkin-Elmer 237 and 257 spectrophotometers. ^1H N.m.r. spectra were determined (for solutions in CCl_4 unless specified otherwise) at 60 MHz with a Perkin-Elmer R10 spectrometer and mass spectra were recorded with A.E.I. MS 902 and MS 12 spectrometers. Rotations were measured for chloroform solutions at 22° with a Bendix polarimeter 143C.

Hydrogenolysis of 3β-*Benzyloxy*-9,10-*epoxy*-5-*methyl*-19-*nor*-5β,10α-*cholestan*-6β-*yl Acetate* (5), 3β-*Benzyloxy*-9,10-*epoxy*-5-*methyl*-19-*nor*-5β,9β-*cholestan*-6β-*yl Acetate* (6), *and* 3β-*Benzyloxy*-5,14-*dimethyl*-18,19-*bisnor*-5β,8α,9β,10α,14β-*cholest*-13(17)-*ene* (10).—An ethyl acetate solution of the steroid was hydrogenated over 10% palladium–charcoal at room temperature until uptake ceased. The solution was filtered and evaporated. The benzyl ether (5) (200 mg) gave 9,10-*epoxy*-3β-*hydroxy*-5-*methyl*-19-*nor*-5β,10α-*cholestan*-6β-*yl acetate* (3) (150 mg), m.p. 128—130° (from methanol), $[\alpha]_D$ 0° (*c* 0·6), $\nu_{max.}$ (KBr) 1740 (AcO) and 3500 cm (OH), τ 4·9—5·3 (m, $W_{\frac{1}{2}}$ *ca.* 18 Hz, 6-H), 5·7—5·9 (m, $W_{\frac{1}{2}}$ *ca.* 9 Hz, 3-H), 8·05 (s, AcO), 8·75 (s, 5-Me), and 9·25 (s, 13-Me) (Found: C, 75·65; H, 10·55. $C_{29}H_{48}O_4$ requires C, 75·6; H, 10·5%).

The benzyl ether (6) (200 mg) gave 9,10-*epoxy*-3β-*hydroxy*-5-*methyl*-19-*nor*-5β,9β-*cholestan*-6β-*yl acetate* (4) (150 mg), m.p. 62—63° (from methanol), $[\alpha]_D$ +81° (*c* 0·6), τ 5·1—5·44 (m, $W_{\frac{1}{2}}$ *ca.* 18 Hz, 6-H), 5·8—6·2 (m, $W_{\frac{1}{2}}$ *ca.* 14 Hz, 3-H), 8·03 (s, AcO), 8·92 (s, 5-Me), and 9·1 (s, 13-Me) (Found: C, 75·0; H, 10·3. $C_{29}H_{48}O_4$ requires C, 75·6; H, 10·5%).

The benzyl ether (10) (450 mg) gave 3β-*hydroxy*-5,14-*dimethyl*-18,19-*bisnor*-5β,8α,9β,10α,14β-*cholest*-13(17)-*en*-6β-*yl acetate* (9) (360 mg), as a gum, $[\alpha]_D$ +17° (*c* 2·3), $\nu_{max.}$ 1740 (AcO), and 3640 cm^{-1} (OH), τ 5·2—5·8 (m, 6-H), 5·8—6·1 (m, 3-H), 8·04 (s, AcO), 8·9 (s, 5-Me), 9·00 and 9·1 (d, *J* *ca.* 6 Hz, 20-Me), and 9·12 (s, 14-Me), M^+ (mass spectrum) 444·3594 ($C_{29}H_{48}O_3$ requires *M*, 444·3603).

Reaction of the 3β-*Hydroxy*-9α,10α-*epoxide* (3), *the* 3β-*Hydroxy*-9β,10β-*epoxide* (4), *and the* 3β-*Hydroxy*-$\Delta^{13(17)}$ *compound* (9) *with Lead Tetra-acetate*.—Solutions of steroid in dry benzene–cyclohexane (1 : 1) and lead tetra-acetate (4 mol. equiv.) were heated under reflux, in nitrogen, for the periods specified; the mixture was filtered and poured into water, and the organic layer was separated and dried. Removal of the solvent gave the crude product, which was purified by preparative t.l.c.

The 3β-hydroxy-9α,10α-epoxide (3) (180 mg) in 2 h gave an oil which after t.l.c. [elution with benzene–ethyl acetate (3 : 1)] gave 9,10-*epoxy*-3β,5-*epoxymethano*-19-*nor*-5β,10α-*cholestan*-6β-*yl acetate* (11) (138 mg), m.p. 115—116° (from methanol), $[\alpha]_D$ −12° (*c* 0·5), $\nu_{max.}$ (KCl) 1740 cm^{-1} (AcO), τ 5·18—5·34 (m, $W_{\frac{1}{2}}$ *ca.* 8 Hz, 6-H), 5·48—5·73 (m, $W_{\frac{1}{2}}$ *ca.* 10 Hz, 3-H), 6·35 (q, J_{AB} *ca.* 8 Hz, 5-CH_2O), 8·05 (s, AcO), and 9·23 (s, 13-Me) (Found: C, 75·75; H, 10·3. $C_{29}H_{46}O_4$ requires C, 75·95; H, 10·1%).

The 3β-hydroxy-9β,10β-epoxide (4) (100 mg) in 4 h gave an oil which after t.l.c. [elution with benzene–ethyl acetate (3 : 1)] gave 9,10-*epoxy*-3β,5-*epoxymethano*-19-*nor*-5β,9β-*cholestan*-6β-*yl acetate* (12) (50 mg), as an oil, $[\alpha]_D$ 0°, $\nu_{max.}$ 1745 cm^{-1} (AcO), τ 4·98—5·83 [q, *J* (apparent) *ca.* 5 and 10 Hz, 6-H], 5·65—5·00 (m, $W_{\frac{1}{2}}$ *ca.* 10 Hz, 3-H), 6·23 (q, J_{AB} *ca.* 8 Hz, 5-CH_2O), 8·02 (s, OAc), and 9·2 (s, 13-Me) (Found: C, 75·95; H, 10·1. $C_{29}H_{46}O_4$ requires C, 75·95; H, 10·1%).

The 3β-hydroxy-$\Delta^{13(17)}$-compound (9) (150 mg) in 2·5 h gave an oil which after t.l.c. [elution (twice) with benzene–ethyl acetate (3 : 1)], gave 3β,5-*epoxymethano*-5,14-*dimethyl*-18,19-*bisnor*-5β,8α,9β,10α,14β-*cholest*-13(17)-*en*-6β-*yl acetate* (13) (67 mg) a gum, $[\alpha]_D$ −15° (*c* 1·3), $\nu_{max.}$ 1745 cm^{-1} (AcO), τ 5·05—5·4 (m, 6-H), 5·7—6·00 (m, 3-H), 6·3 (t, *J* *ca.* 8 Hz, 5-CH_2O), 8·0 (s, AcO), 9·00 and 9·10 (d, *J* *ca.* 6 Hz, 20-Me), and 9·15 (s, 14-Me) (Found: C, 78·7; H, 10·45. $C_{29}H_{46}O_3$ requires C, 78·7; H, 10·45), and starting material (9) (30 mg).

Preparation of Nitrite Esters (7) *and* (8).—Nitrosyl chloride was bubbled into a solution of steroid in pyridine (100 ml per g) for 4 min at −20°. The mixture was then poured onto ice and extracted with ether. The ethereal layer was then dried and the solvent evaporated.

The 3β-hydroxy-9α,10α-epoxide (3) (190 mg) gave an oil which after t.l.c. [elution with benzene–ethyl acetate (3 : 1)] gave 9,10-epoxy-5-methyl-6β-acetoxy-19-nor-5β,10α-cholestan-3β-yl nitrite (7) (150 mg), as a gum, $\nu_{max.}$ 1650 (O–N=O) and 1745 cm^{-1} (AcO), τ 4·1—4·35 (m, 3-H), 4·9—5·3 (m, 6-H), 8·05 (s, OAc), 8·9 (5-Me), and 9·22 (s, 13-Me).

The 3β-hydroxy-9β,10β-epoxide (4) (500 mg) gave 6β-acetoxy-9,10-epoxy-5-methyl-19-nor-5β,9β-cholestan-3β-yl nitrite (8) (500 mg), which was photolysed without purification.

Photolysis of Nitrite Esters (7) *and* (8).—Solutions of the steroid in dry benzene (80 ml), in nitrogen, were irradiated for 2 h in a water-cooled quartz apparatus using a medium pressure mercury lamp (125 W).

Nitrite ester (7) (1·0 g) gave an oil, which after t.l.c. [elution with benzene–ethyl acetate (3 : 1)], gave 9,10-*epoxy*-5-*methyl*-3-*oxo*-19-*nor*-5β,10α-*cholestan*-6β-*yl acetate* (15) (180 mg), m.p. 122—123° (from methanol), $[\alpha]_D$ +5·3° (*c* 0·9), $\nu_{max.}$ 1720 and 1740 cm^{-1} (3-C=O and AcO), τ 4·8—5·2 (m, 6-H), 8·05 (s, AcO), 9·0 (s, 5-Me), and 9·25 (s, 13-Me) (Found: C, 75·9; H, 10·05. $C_{29}H_{46}O_4$ requires C, 75·9; H, 10·1%), and two more polar mixtures. Further t.l.c. of the less polar of these (338 mg) [elution with benzene–ethyl acetate (10 : 1)], gave the ether (11) (22 mg), 9,10-epoxy-3β-hydroxy-5-nitro-oxymethyl-19-nor-5β,10α-cholestan-6β-yl acetate (17) (64 mg), $\nu_{max.}$ 1645 and 1287 (O–NO_2), 1750 (AcO), and 3650br cm^{-1} (OH), τ 4·95 (q, J_{AB} *ca.* 12 Hz, 5-CH_2), 4·9—5·2 (m, $W_{\frac{1}{2}}$ *ca.* 20 Hz, 6-H), 5·6—5·9 (m, $W_{\frac{1}{2}}$ *ca.* 10 Hz, 3-H), 8·02 (s, AcO), and 9·20 (s, 13-Me), and the 3β-hydroxy-9α,10α-epoxide (3) (153 mg). Further t.l.c. of the more polar mixture (470 mg) [elution with ethyl acetate], gave 9,10-*epoxy*-3β-*hydroxy*-5-[(E)-*hydroxyiminomethyl*]-19-*nor*-5β,10α-*cholestan*-6β-*yl acetate* (19) (43 mg), m.p. 198—199° (from chloroform–hexane), $[\alpha]_D$ +44° (*c* 1·4), $\nu_{max.}$ 1740 (AcO), and 3600—3100br cm^{-1} (OH), τ ($CDCl_3$) 2·35 (s, CH=NOH), 4·8—5·1 (m, 6-H), 5·7—6·0 (m, 3-H), 8·02 (s, AcO), and 9·22 (s, 13 Me) (Found: C, 71·15; H, 9·6. $C_{29}H_{47}NO_5$ requires C, 71·15; H, 9·7%), and 9,10-*epoxy*-3β-*hydroxy*-5[(Z)-*hydroxyiminomethyl*]-19-*nor*-5β,10α-*cholestan*-6β-*yl acetate* (20) (110 mg), m.p. 100° (amorphous solid), $[\alpha]_D$ 36·6° (*c* 1·9), $\nu_{max.}$ 1750 (AcO), 3600—3300 and 3650 cm^{-1} (OH), τ 2·8 (s, CH=NOH), 4·4—4·9 (m, 6-H), 5·6—6·1 (m, 3-H), 7·92 (AcO), and 9·3 (s, 13-Me), M^+ (mass spectrum) 489·3463 ($C_{29}H_{47}NO_5$ requires *M*, 489·3454).

The nitrite ester (8) (500 mg) gave an oil which after preparative t.l.c. [elution with benzene–ethyl acetate (3 : 1)], gave 9,10-epoxy-5-methyl-3-oxo-19-nor-5β,9β-cholestan-6β-yl acetate (16) (50 mg), as a gum, $[\alpha]_D$ +19° (*c* 1·0), $\nu_{max.}$ 1720 and 1740 cm^{-1} (3-C=O and AcO), τ 5·3—5·6 [q, *J* (apparent)

10 and 5 Hz, 6-H], 8·05 (s, AcO), 8·9 (s, 5-Me), and 9·2 (s, 13-Me), the 3β-hydroxy-9β,10β-epoxide (4) (90 mg), and 9,10-*epoxy*-3β-*hydroxy*-5[(E)-*hydroxyiminomethyl*]-19-*nor*-5β,9β-*cholestan*-6β-*yl acetate* (21) (50 mg), as a gum, $[\alpha]_D$ +104° (*c* 0·6), τ 2·5 (s, CH=NOH), 5·1—5·6 (m, 6-H), 5·8—6·1 (m, 3-H), 8·05 (s, AcO), and 9·2 (s, 13-Me), M^+ (mass spectrum) 489 ($C_{29}H_{47}NO_5$ requires *M*, 489).

9,10-*Epoxy*-5-*nitro-oxymethyl*-19-*nor*-5β,10α-*cholestane*-3β,6β-*diyl Diacetate* (18).—Acetylation of the 3β-hydroxy-5β-hydroxymethyl nitrate (17) (64 mg) with an excess of acetic anhydride in pyridine followed by the normal work-up gave the *diacetoxy*-5β-*hydroxymethyl nitrate* (18) (60 mg), as a gum, $[\alpha]_D$ +37° (*c* 1·2), $\nu_{max.}$ 1645 and 1285 (O–NO_2), and 1750 cm^{-1} (AcO), τ 4·6—5·3 (m, 3- and 6-H), 5·15 (q, J_{AB} *ca.* 12 Hz, 5-CH_2O), 8·0—8·05 (AcO), and 9·22 (Found: C, 69·9; H, 9·15. $C_{31}H_{49}NO_6$ requires C, 70·0; H, 9·3%).

9,10-*Epoxy*-3α,5-*methano*-4-*oxa*-A-*homo*-19-*nor*-5α,10α-*cholestane*-6β,4aξ-*diyl Diacetate* (22) *and* 9,10-*Epoxy*-3α,5-*methano*-4-*oxa*-A-*homo*-19-*nor*-5α,9β-*cholestane*-6β,4aξ-*diyl Diacetate* (23).—A solution of the steroid in acetic acid (*ca.* 10 mg ml^{-1}) was treated at 5° with an excess of a solution of sodium nitrite in acetic acid (*ca.* 10 mg ml^{-1}). After 10 min, the mixture was poured into water and extracted with ether. After drying, the solvents were evaporated off to give the crude product.

The *E*-oxime (19) (50 mg) gave after t.l.c. [elution with benzene–ethyl acetate (3 : 1)], the *hemiacetal acetate* (22) (16 mg), $\nu_{max.}$ 1750 cm^{-1} (AcO), τ 3·88 (s, O–CH–OAc), 5·2—5·5 (m, 3- and 6-H), 8·12 (s, 2 × AcO), and 9·25 (s, 13-Me), M^+ (mass spectrum) 516·3461 ($C_{31}H_{48}O_6$ requires *M*, 516·3451).

The *E*-oxime (21) (35 mg) gave after t.l.c. [elution with benzene–ethyl acetate (3 : 1)], the *hemiacetal acetate* (23) (15 mg), $\nu_{max.}$ 1750 cm^{-1} (AcO), τ 3·78 (s, O–CH–OAc), 5·1—5·35 (m, 6-H), 5·35—5·6 (m, 3-H), 8·1 (s, 2 × AcO), 9·18 (s, 13-Me), M^+ (mass spectrum) 516 ($C_{31}H_{48}O_6$ requires *M*, 516).

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