Steroidal *N*-Nitroamines. Part 1. Denitroamination of Steroidal 4β-, 6β-, 7α-, and 7β-Nitroamines

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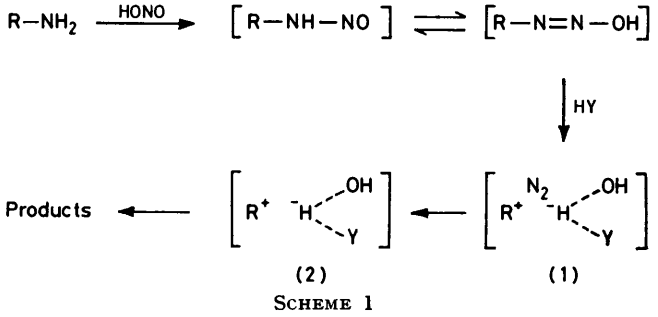
The α-hydroxy-nitroamines 6β-nitroamino-5α-cholestane-3β,5α-diol (26) and 6β- and 4β-nitroamino-5α-cholestan-5α-ol (27) and (30) have been prepared by reactions of cholest-5-en-3β-yl formate, cholest-5-ene, and cholest-4-ene with nitrous acid and boron trifluoride–ether complex, and subsequent treatment with sodium borohydride. The nitroimines (12) and (25), obtained by nitrosation of the corresponding oximes, undergo similar reduction to yield 6β-nitroamino-5α-cholestan-3β-yl acetate (32) and the 7β- and 7α-nitroaminocholest-5-en-3β-yl acetates (36) and (38). The results of denitroamination reactions of these nitroamines, performed with acetic anhydride and pyridine, are consistent with a mechanism involving a nitrous oxide-separated ion-pair intermediate (6). The nitroamines (26), (27), and (30) gave the corresponding 5α- and 4α-oxirans (28), (29), and (31) by intramolecular nucleophilic substitution. The nitroamine (32) yields, by a hydrogen β-elimination, the acetyl derivatives of cholest-4-en-3β-ol (33), cholest-5-en-3β-ol (34), and cholest-6-en-3β-ol (35). The acetates of cholest-5-ene-3β,7β-diol (37) and cholest-5-ene-3β,7α-diol (39) were obtained from the 7β- and 7α-nitroamines (36) and (38) through substitution by a counter-ion, a total retention of configuration for the 7α-nitroamine and 14% inversion for the 7β-isomer being observed.

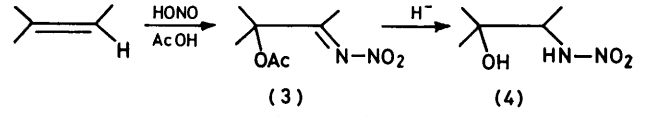
N-NITROSO-AMINES have long been postulated as intermediates during the deamination of aliphatic primary amines with nitrous acid.[1] The currently accepted mechanism for the deamination [2] involves formation



SCHEME 1

of a nitrogen-separated ion pair (1) (Scheme 1) that after ejection of nitrogen gives a solvated ion pair (2) which collapses to the products.†

The behaviour of these ion pairs has been studied extensively, and the reaction products have been



SCHEME 2

shown to be dependent on both the *C*-amino stereochemistry and the deamination reaction conditions.[2] The products can be explained in terms of three general types of reaction of these ion pairs: substitution, β-elimination, and rearrangement.

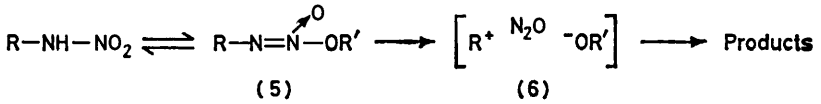
† Recently, mechanistic studies of axial and equatorial 4-t-butylcyclohexylamines [3] and *trans*-2-decalylamines [4] have been reported.

We had previously [5] prepared several α-acetoxy-*N*-nitro-imines (3), by treatment of trisubstituted steroid olefins with sodium nitrite and boron trifluoride–ether complex in acetic acid (Scheme 2); since reduction of *N*-nitro-imines with metal hydrides leads to *N*-nitro-amines (4) in good yields,[6] this allowed us to prepare several stable steroid *N*-nitro-amines. We were then able to compare the chemical behaviour of these materials with that of the aforementioned *N*-nitroso-amines.

It has long been known that *N*-nitro-amines exist partially as the tautomeric azoxy-compounds (5; R′ = H) (*aci*-nitro-amines), as illustrated by the isolation of *O*-alkyl derivatives (5; R′ = alkyl) during the alkylation of *N*-nitro-amines [7] (Scheme 3). Hence, there is the possibility of formation from (5; R′ = H) of a nitrous oxide-separated ion-pair (6; R′ = H), which, after expulsion of N_2O, collapses to yield the reaction products.

Not much is known about the denitroamination of aliphatic primary nitroamines, although it was reported at the end of the last century that acid treatment of some simple nitroamines leads to alkenes and alcohols.[7b,c] Ejection of N_2O during denitroamination of *N*-nitro-amides and *N*-nitrocarbamates has been reported also,[8] and, similarly, intermediates like (5; R′ = CO-alkyl and R′ = OCO-alkyl, respectively) have been postulated.

In the present paper we describe the behaviour of several steroid *N*-nitro-amines on denitroamination with acetic anhydride and pyridine.

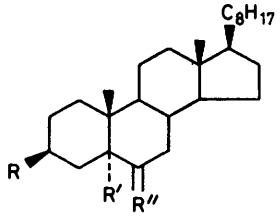


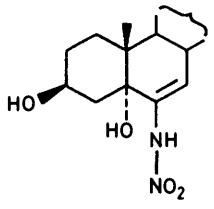
SCHEME 3

RESULTS AND DISCUSSION

Preparation of the Substrates.—6-Nitroimino-5α-cholestane-3β,5-diol diformate (7) was obtained (73%) by treatment, at 0 °C, of cholesteryl formate with sodium

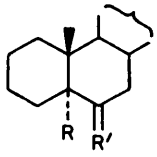
nitrite in formic acid in the presence of boron trifluoride–ether complex. In addition, small amounts (5%) of the hydrolysis product, 6-oxo-5α-cholestane-3β,5-diol diformate (8), were obtained. We have previously described [5b] the synthesis of α-acetoxy-nitroimines by similar treatment of steroid olefins but with acetic acid as nucleophile. When formic acid is used instead of acetic acid the reaction goes smoothly with better yields. The i.r. spectrum of compound (7) exhibits bands characteristic of the nitroimine group [6c] at 1 635 (C=N) and 1 575 and 1 315 cm^{-1} (NO_2), and the n.m.r. spectrum shows the

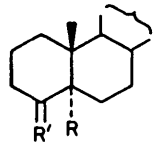




(7) R = R′ = HCO_2, R″ = N–NO_2
(8) R = R′ = HCO_2, R″ = O
(9) R = R′ = OH, R″ = O
(10) R = OAc, R′ = H, R″ = O
(11) R = OAc, R′ = H, R″ = N–OH
(12) R = OAc, R′ = H, R″ = N–NO_2

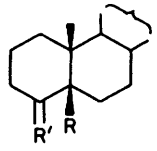
(13)

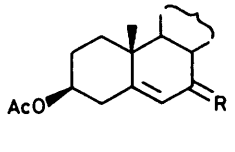




(14) R = HCO_2, R′ = N–NO_2
(15) R = HCO_2, R′ = O
(16) R = OH, R′ = O

(17) R = HCO_2, R′ = N–NO_2
(18) R = HCO_2, R′ = O
(19) R = OH, R′ = O





(20) R = HCO_2, R′ = N–NO_2
(21) R = HCO_2, R′ = O
(22) R = OH, R′ = O

(23) R = O
(24) R = N–OH
(25) R = N–NO_2

SCHEME 4

presence of two formyl groups (singlets at δ 8.00 and 8.14). Chemical support for this structure was obtained by mild hydrolysis of (7) with potassium hydroxide–methanol, to yield the known [9] ketone (9) and the vinylnitroamine (13).

The diformyl ketone (8) (δ 8.02 and 8.12) was transformed into the dihydroxy-ketone (9) by adsorption on neutral aluminium oxide.

The reaction of cholest-4-ene with sodium nitrite and formic acid in the presence of boron trifluoride–ether complex leads to a mixture of 4-nitroimino-5α-cholestan-5-yl formate (17) (40%), 4-nitroimino-5β-cholestan-5-yl formate (20) (5%), 4-oxo-5α-cholestan-5-yl formate (18) (20%), 4-oxo-5β-cholestan-5-yl formate (21) (10%), and smaller amounts of 6-nitroimino-5α-cholestan-5-yl formate (14) (3%) and 6-oxo-5α-cholestan-5-yl formate (15) (3%). Similar treatment of cholest-5-ene gave a mixture of nitroimines (14) (26%), (17) (16%), and ketones (15) (5%), (18) (12%), and (21) (9%). The production of both C-6 and C-4 oxidized products from either cholest-4-ene or cholest-5-ene shows that under the acidic conditions of the reaction an equilibrium is established between the two olefins. This equilibration is not observed when the reaction is performed with acetic acid [5b] instead of formic acid as solvent, nor with cholesteryl formate as starting material. The spectroscopic data are in agreement (see Experimental section) with the structures proposed for these substances. Chemical support was obtained through hydrolysis over neutral aluminium oxide (activity III) of the formyl nitroimines and the formyl ketones, yielding the previously described hydroxy-ketones [10] (16), (19), and (22).

The reduction [6] of the formyl nitroimines (7), (14), and (17) with sodium borohydride–ethanol or lithium aluminium hydride–diethyl ether, at room temperature, leads to 6β-nitroamino-5α-cholestane-3β,5-diol (26), 6β-nitroamino-5α-cholestan-5-ol (27), and 4β-nitroamino-5α-cholestan-5-ol (30), respectively, in yields of about 70%.

The nitroamine (30) exhibits i.r. absorptions at 3 410 (NH) and 1 580 cm^{-1} (NO_2), and an n.m.r. multiplet at δ 8.5 ($W_{\frac{1}{2}}$ 30 Hz) corresponding to the amine proton, exchangeable with deuterium oxide. Furthermore, the mass spectrum clearly indicates the presence of a nitroamine function, showing fragments corresponding to $M^+ - NO_2$ (*m/z* 402, 10%) and $M^+ - NH_2NO_2$ (*m/z* 386, 100%). The shape of the n.m.r. signal at δ 4.20 ($W_{\frac{1}{2}}$ 9 Hz) corresponding to H-4, establishes the axial configuration of the nitroamine group. The structures of the other two nitroamines (26) and (27) were deduced by similar considerations.

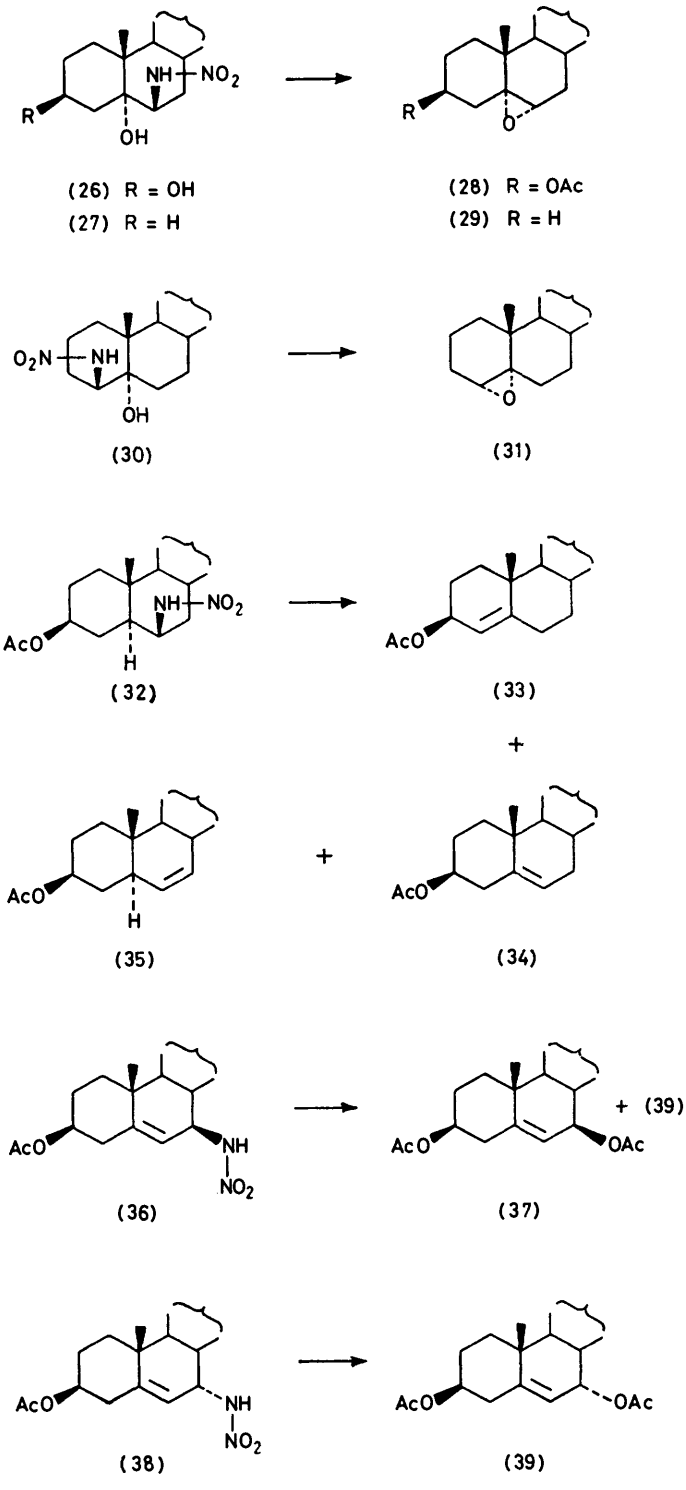
6β-Nitroamino-5α-cholestan-3β-yl acetate (32) was prepared from the ketone (10); this was transformed into its oxime (11), which was treated with sodium nitrite in acetic acid–methylene chloride to give the nitroimine (12). This is a non-crystalline, unstable substance, easily hydrolysed to the starting ketone (10), and showing i.r. absorptions at 1 625 (C=N) and 1 560 cm^{-1} (NO_2). Reduction of this nitroimine with sodium borohydride yields the nitroamine (32), identified by spectroscopic data (see Experimental section).

The C-7 epimeric nitroamines (36) and (38) were obtained from 7-oxocholesteryl acetate (23), through formation of the oxime (24) and subsequent reaction with

nitrous acid and reduction with sodium borohydride The nitroimine (25) has characteristic i.r. absorptions at 1 630, 1 550 and 1 310 cm^{-1}, and in the ^1H n.m.r. spectrum the H-6 signal is a singlet at δ 5.82. ^{13}C N.m.r. values also agree with this structure; thus, C-5 and C-7 signals appear as singlets at 170.0 and 164.7 p.p.m., respectively, and that for C-6 as a doublet at 114.7 p.p.m. Sodium borohydride reduction of (25) gave a mixture (*ca.* 1 : 1) of 7β- (36) and 7α-nitroaminocholest-5-en-3β-yl acetate (38). Elemental analysis and spectral data are in good agreement with the proposed stereoisomeric structures, which are distinguished by C-6 vinylic proton n.m.r. signals [broad singlet at δ 5.30 ($W_{\frac{1}{2}}$ 5 Hz, equatorial nitroamine) for (36); doublet at δ 5.57 (J 5 Hz, axial nitroamine) for (38)].*

Denitroamination Reactions.—The denitroamination of the α-hydroxy-nitroamines (26), (27), and (30) was performed at room temperature by treatment with acetic anhydride and pyridine for 12 h, to give exclusively the oxirans (28), (29), and (31), respectively, in yields of 70—80%. It seems reasonable to consider the reaction as leading selectively to nitrous oxide-separated ion pairs, like the postulated nitrogen-separated ion pairs in the deamination of primary amines with nitrous acid.[2] The departure of nitrous oxide with concomitant attack from the rear by the neighbouring hydroxy-group produces the corresponding oxirans. This reaction is possible because the axial configuration of the nitroamine group permits rear-side attack by the axial 5α-oxygen substituent. It is of interest that the expected products of substitution by the counter-ion (6- or 4-acetyl derivatives) or, in view of the axial configuration of the starting nitroamines (see below), from β-hydrogen elimination (3- or 6-didehydro-derivatives) are not observed. This indicates that intramolecular nucleophilic substitution is kinetically highly favoured. Similar behaviour is observed in the nitrous acid deamination of *trans*-diaxial α-hydroxy-amines.[11] Nevertheless, unexpectedly, deaminations in aqueous acetic acid of 4β- and 6β-amino-5α-cholestan-5-ol gave small amounts of 4β-hydroxycholest-5-ene and 6β-hydroxycholest-4-ene, respectively, with cholesta-3,5-diene as major product in both reactions.[12] Intramolecular stereochemical inversion of the cation of the ion pair, to produce a *cis*-relationship between the ion pair and the hydroxy-group, is unlikely because no products from a Tiffaneau–Demjanov-type rearrangement have been isolated in these examples.

In the deamination of 6β-nitroamino-5α-cholestan-3β-yl acetate (32), which has no hydroxy-group α to the nitroamine group, the olefins (34), (35), and (33) are formed in 5 : 1 : 2 ratio; the first two compounds are produced by hydrogen β-elimination and the last through a 1,2-hydride shift [3] from the angular C-5 position to form a tertiary carbocation subsequently stabilized by hydrogen β-elimination. This agrees with



SCHEME 5

the almost exclusive formation of olefins by deamination of axial amines *via* a base-induced *trans*-mechanism.[2a,4b,13]

With the 7β- and 7α-nitroamines (36) and (38) substitution takes place to give (37) and (39), total retention of configuration for the pseudoaxial 7α-nitroamine being observed, while 14% inversion is found for the pseudo-

* $J_{6,7}$ Values calculated from measurements of Dreiding stereomodels are 0 for (36) and 6 Hz for (38).

equatorial 7β-isomer. The high degree of retention observed for the axial nitroamine is surprising, as also is the fact that no β-elimination occurs, although the latter circumstance must be related with the steric hindrance of the proton at C-8. In contrast, Shoppee *et al.*[2g] have reported that β-elimination predominates (70%) during the nitrous acid deamination of 7α-aminocholest-5-en-3β-ol to give cholesta-5,7-dien-3β-ol.

All the denitroamination reactions reported here are consistent with the mechanism shown in Scheme 3. The equilibrium between nitroamine and *aci*-nitro-amine [7] (5; R′ = H) is shifted under the reaction conditions (acetic anhydride–pyridine) to produce the unstable *O*-acetyl-*aci*-nitro-amines * (5; R′ = Ac) which decompose to give the N_2O-separated ion pairs (6; R′ = Ac) that can undergo reaction in various ways: intramolecular substitution if a nucleophile is conveniently positioned in the molecule, substitution by the counter-ion with predominant retention of configuration, and hydrogen β-elimination to produce olefins.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus, and are corrected. Optical rotations were measured for solutions in $CHCl_3$. ^1H N.m.r. spectra were recorded with a Perkin-Elmer R-12B (60 MHz) or a R-32 (90 MHz) instrument for solutions in $CDCl_3$ with Me_4Si as internal reference. ^{13}C N.m.r. data were measured at 20 MHz for solutions in $CDCl_3$ with a Varian C.F.T.-20 instrument and mass spectra were recorded with a VG Micromass ZAB-2F spectrometer. T.l.c. was performed on Merck silica gel 60, and column chromatography on Merck silica gel 0.063—0.2 mm. The spray reagent for t.l.c. was H_2SO_4–AcOH–H_2O (1 : 20 : 4).

6-Nitroimino-5α-cholestane-3β,5-diol Diformate (7).—To a solution of *cholesteryl formate* (1.7 g) in methylene chloride (150 ml) containing formic acid (30 ml) and boron trifluoride–ether (1.5 ml), sodium nitrite (1.7 g) was added in portions at 0 °C during 30 min. The mixture was stirred for an additional 1 h at 0 °C. After the addition of water, the solution was extracted with chloroform and then the organic layer washed with aq. $NaHCO_3$ and water, dried (Na_2SO_4) and evaporated under vacuum. Column chromatography of the crude product (benzene–ethyl acetate 98 : 2 as eluant) afforded *6-nitroimino-5α-cholestane-3β,5-diol diformate* (7) (1.55 g) and *6-oxo-5α-cholestane-3β,5-diol diformate* (8) (0.1 g). The nitroimine (7) had m.p. 137—139 °C (MeOH), $[\alpha]_D$ −49° (*c* 0.23); *m/z* 473 (21%, $M^+ - HCO_2$), 428 (42%, $M^+ - 2HCO_2$), and 427 (16%, $M^+ - HCO_2 - NO_2$); $\nu_{max.}$ ($CHCl_3$) 1 725, 1 635, 1 575, and 1 315 cm^{-1}; δ 8.14 (1 H, s, 5-CO_2H), 8.00 (1 H, s, 3-CO_2H), 4.95 (1 H, m, $W_{\frac{1}{2}}$ 24 Hz, 3α-H), 1.02 (3 H, s, 10-Me), 0.85 (6 H, d, *J* 6 Hz, 25-Me_2), and 0.63 (3 H, s, 13-Me) (Found: C, 67.15; H, 8.95; N, 5.4. $C_{29}H_{46}N_2O_6$ requires C, 67.3; H, 8.9; N, 5.35%). The ketone (8) had m.p. 136—138 °C (n-hexane), $[\alpha]_D$ −21° (*c* 0.21); *m/z* 474 (7%, M^+), 446 (20%, $M^+ - CO$), 428 (44%, $M^+ - HCO_2H$), and 382 (100%, $M^+ - 2HCO_2H$); $\nu_{max.}$ ($CHCl_3$) 1 720 cm^{-1}; δ 8.12 (1 H, s, 5-HCO_2), 8.02 (1 H, s, 3-HCO_2), 4.9 (1 H, m, $W_{\frac{1}{2}}$ 24 Hz, 3α-H), 0.86 (3 H, s, 10-Me), 0.85 (6 H, d, *J* 6 Hz, 25-Me_2), and 0.64 (3 H, s, 13-Me) (Found: C, 73.3; H, 9.65. $C_{29}H_{46}O_5$ requires C, 73.4; H, 9.75%).

Reaction of 6-Nitroimino-5α-cholestane-3β,5-diol Diformate (7) with Potassium Hydroxide.—A solution of the nitroimine (7) (0.5 g) and potassium hydroxide (0.6 g) in methanol (60 ml) was stirred at ambient temperature for 2 h. The mixture was poured into aqueous hydrochloric acid (10%) and extracted with ethyl acetate. Usual work-up gave a residue which was chromatographed (benzene–ethyl acetate 2 : 3 as eluant) to yield 6-oxo-5α-cholestane-3β,5-diol (9) (0.19 g) and 6-nitroamino-5α-cholest-6-ene-3β,5-diol (13) (0.21 g). The ketone (9) had m.p. 225—227 °C (n-hexane), $[\alpha]_D$ −34° (*c* 0.26) (lit.,[9a,b] m.p. 230—232 °C, $[\alpha]_D$ −33°); *m/z* 418 (100%, M^+), 400 (19%, $M^+ - H_2O$), and 382 (4%, $M^+ - 2H_2O$); $\nu_{max.}$ ($CHCl_3$) 3 400 and 1 700 cm^{-1}; δ 3.95 (1 H, m, $W_{\frac{1}{2}}$ 24 Hz, 3α-H), 0.85 (6 H, d, *J* 6 Hz, 25-Me_2), 0.80 (3 H, s, 10-Me), and 0.63 (3 H, s, 13-Me) (Found: C, 77.6; H, 11.0. Calc. for $C_{27}H_{46}O_3$: C, 77.45; H, 11.05%). The nitroamine (13) had m.p. 168—170 °C (MeOH), $[\alpha]_D$ −59° (*c* 0.22) (lit.,[9c] m.p. 178—180 °C); *m/z* 462 (5%, M^+), 417 (55%), 416 (100%, $M^+ - NO_2$), 415 (56%), 400 (70%, $M^+ - NO_2NH_2$), and 398 (45%, $M^+ - NO_2 - H_2O$); $\nu_{max.}$ ($CHCl_3$) 3 560, 3 360, 1 580, and 1 310 cm^{-1}; δ ([$^2H_6$]acetone) 5.89 (1 H, m, $W_{\frac{1}{2}}$ 4 Hz, 7-H), 4.0 (1 H, m, $W_{\frac{1}{2}}$ 24 Hz, 3α-H), 0.99 (3 H, s, 10-Me), 0.92 (3 H, d, *J* 6 Hz, 20-Me), 0.87 (6 H, d, *J* 6 Hz, 25-Me_2), and 0.77 (3 H, s, 13-Me) (Found: C, 70.15; H, 10.0; N, 6.1. Calc. for $C_{27}H_{46}N_2O_4$: C, 70.1; H, 10.0; N, 6.05%).

6-Oxo-5α-cholestane-3β,5-diol (9).—A solution of 6-oxo-5α-cholestane-3β,5-diol diformate (8) (0.05 g) in benzene (5 ml) was adsorbed over neutral alumina (grade III) for 12 h. Extraction with chloroform yielded the previously described compound (9) (0.04 g).

6β-Nitroamino-5α-cholestane-3β,5-diol (26).—To a solution of 6-nitroimino-5α-cholestane-3β,5-diol diformate (7) (2.27 g) in absolute ethanol (160 ml), sodium borohydride (2 g) was added and the mixture was stirred at ambient temperature for 1.5 h. Usual work-up and column chromatography (benzene–ethyl acetate 3 : 2 as eluant) gave the non-crystalline *6β-nitroamino-5α-cholestane-3β,5-diol* (26) (1.6 g); *m/z* 418 ($M^+ - NO_2$) and 402 ($M^+ - NH_2NO_2$); $\nu_{max.}$ ($CHCl_3$) 3 580, 3 480, 1 570, and 1320 cm^{-1}; δ 4.05 (2 H, m, $W_{\frac{1}{2}}$ 30 Hz, 3α-H, 6α-H), 0.92 (3 H, s, 10-Me), 0.87 (6 H, d, *J* 6 Hz, 25-Me_2), and 0.66 (3 H, s, 13-Me) (Found: C, 69.7; H, 10.6; N, 5.95. $C_{27}H_{48}N_2O_4$ requires C, 69.8; H, 10.4; N, 6.05%).

Reaction of Cholest-4-ene with Nitrous Acid and Boron Trifluoride–Ether.—To a solution in methylene chloride (150 ml) of cholest-4-ene (3 g), formic acid (25 ml), and boron trifluoride–ether complex (2 ml), sodium nitrite (3 g) was added in portions at 0 °C during 1 h. The mixture was then stirred at 0 °C for 2 h and worked up as usual. Column chromatography of the crude product (benzene–n-hexane 4 : 1 as eluant) afforded *6-nitroimino-5α-cholestan-5-yl formate* (14) (3%), *4-nitroimino-5α-cholestan-5-yl formate* (17) (40%), *4-nitroimino-5β-cholestan-5-yl formate* (20) (5%), *6-oxo-5α-cholestan-5-yl formate* (15) (3%), *4-oxo-5β-cholestan-5-yl formate* (21) (10%), and *4-oxo-5α-cholestan-5-yl formate* (18) (20%).

The nitroimine (14) crystallized from methanol, m.p. 112—113 °C, $[\alpha]_D$ −33° (*c* 0.26); *m/z* 428 (3%, $M^+ - NO_2$), 400 (16%), 383 (24%), and 370 (100%); $\nu_{max.}$ (KBr) 1 725, 1 630, and 1 565 cm^{-1}; δ (CCl_4) 8.02 (1 H, s, HCO_2), 0.99 (3 H, s, 10-Me), 0.85 (6 H, d, *J* 6 Hz, 25-Me_2), and 0.67 (3 H,

* Notwithstanding that *O*-alkyl-*aci*-nitro-amines are usually isolable, we could not isolate the proposed intermediates in the deamination reactions.

s, 13-Me) (Found: C, 70.65; H, 9.7; N, 5.85. $C_{28}H_{46}N_2O_4$ requires C, 70.85; H, 9.75; N, 5.9%).

The nitroimine (17) crystallized from chloroform–methanol, m.p. 166—168 °C, $[\alpha]_D$ +121° (*c* 0.18); *m/z* 428.3507 (3%, $C_{28}H_{46}NO_2$ 428.3528), 400.3594 (12%, $C_{27}H_{46}NO$ 400.3580), 382.3479 (68%, $C_{27}H_{44}N$ 382.3474), and 370.3550 (14%, $C_{27}H_{46}$ 370.3500); $\nu_{max.}$ (KBr) 1 720, 1 625, and 1 560 cm^{-1}; δ (CCl_4) 8.04 (1 H, s, HCO_2), 1.00 (3 H, s, 10-Me), 0.86 (6 H, d, *J* 6 Hz, 25-Me_2), and 0.68 (3 H, s, 13-Me) (Found: C, 70.6; H, 9.85; N, 5.85. $C_{28}H_{46}N_2O_4$ requires C, 70.85; H, 9.75; N, 5.9%).

The nitroimine (20) crystallized from chloroform–methanol, m.p. 131—133 °C, $[\alpha]_D$ − 35° (*c* 0.21); *m/z* 428 (11%, $M^+ - NO_2$), 400 (3%), 383 (21%), 382 (40%), and 370 (6%); $\nu_{max.}$ (KBr) 1 715, 1 620, and 1 560 cm^{-1}; δ (CCl_4) 8.01 (1 H, s, HCO_2), 1.13 (3 H, s, 10-Me), 0.86 (6 H, d, *J* 6 Hz, 25-Me_2), and 0.64 (3 H, s, 13-Me) (Found: C, 70.45; H, 9.6; N, 5.85. $C_{28}H_{46}N_2O_4$ requires C, 70.85; H, 9.75; N, 5.9%).

The ketone (15) crystallized from methanol, m.p. 157—159 °C, $[\alpha]_D$ −11° (*c* 0.10); *m/z* 430 (11%, M^+), 384 (50%, $M^+ - HCO_2H$), and 369 (25%); $\nu_{max.}$ (KBr) 1 720 cm^{-1}; δ(CCl_4) 7.99 (1 H, s, HCO_2), 0.86 (6 H, d, *J* 6 Hz, 25-Me_2), 0.79 (3 H, s, 10-Me), and 0.64 (3 H, s, 13-Me) (Found: C, 78.0; H, 10.75. $C_{28}H_{46}O_3$ requires C, 78.10; H, 10.75%).

The ketone (21) crystallized from methanol, m.p. 120—121 °C, $[\alpha]_D$ +18° (*c* 0.20); *m/z* 430.3458 (8%, $C_{28}H_{46}O_3$ 430.3447), 384.3408 (72%, $C_{27}H_{44}O$ 384.3392), and 369 (25%); $\nu_{max.}$ (KBr) 1 720 cm^{-1}; δ (CCl_4) 7.92 (1 H, s, HCO_2), 1.10 (3 H, s, 10-Me), 0.86 (6 H, d, *J* 6 Hz, 25-Me_2), and 0.63 (3 H, s, 13-Me) (Found: C, 78.1; H, 10.65. $C_{28}H_{46}O_3$ requires C, 78.1; H, 10.75%).

The ketone (18) crystallized from methanol, m.p. 159—160 °C, $[\alpha]_D$ +45° (*c* 0.21); *m/z* 430 (4%, M^+), 384 (100%, $M^+ - HCO_2H$), and 369 (38%); $\nu_{max.}$ (KBr) 1 725 and 1 715 cm^{-1}; δ (CCl_4) 8.00 (1 H, s, HCO_2), 0.86 (6 H, d, *J* 6 Hz, 25-Me_2), 0.82 (3 H, s, 10-Me), and 0.65 (3 H, s, 13-Me) (Found: C, 78.2; H, 10.8. $C_{28}H_{46}O_3$ requires C, 78.1; H, 10.75%).

General Procedure for Hydrolysis of the Formyl Nitroimines (14), (17), *and* (20) *and ketones* (15), (18), *and* (21).—Neutral alumina (activity II—III; 10 g) was added to a solution of the nitroimine or ketone (0.1 g) in benzene (7 ml), and the mixture was kept at room temperature for 24 h. Ethyl acetate was then added and the mixture was filtered and evaporated under vacuum. Products were purified by column chromatography (benzene–ethyl acetate 97 : 3 as eluant).

The hydrolysis of the formates (14) and (15) gave 6-oxo-5α-cholestan-5-ol (16) in 90 and 86% yield, respectively, m.p. 151—152 °C (from methanol), $[\alpha]_D$ −38° (*c* 0.19) (lit.,[10a] m.p. 153 °C); *m/z* 402 (100%, M^+), 384 (45%), $M^+ - H_2O$), 369 (31%), and 318 (83%); $\nu_{max.}$ (KBr) 3 500 and 1 695 cm^{-1}; δ(CCl_4) 0.86 (6 H, d, *J* 6 Hz, 25-Me_2), 0.73 (3 H, s, 10-Me), and 0.65 (3 H, s, 13-Me) (Found: C, 80.55; H, 11.5. Calc. for $C_{27}H_{46}O_2$: C, 80.7; H, 11.4%).

The hydrolysis of the formates (17) and (18) yielded 4-oxo-5α-cholestan-5-ol (19) in 76 and 95% yield, respectively, m.p. 161—163 °C (from methanol), $[\alpha]_D$ +59° (*c* 0.33) (lit.,[10b] m.p. 158—161 °C, $[\alpha]_D$ +58°); *m/z* 402 (4%, M^+), 356 (30%), and 332 (60%); $\nu_{max.}$ (KBr) 3 460 and 1 695 cm^{-1}; δ(CCl_4) 0.86 (6 H, d, *J* 6 Hz, 25-Me_2), 0.75 (3 H, s, 10-Me), and 0.64 (3 H, s, 13-Me) (Found: C, 80.8; H, 11.4. Calc. for $C_{27}H_{46}O_2$: C, 80.7; H, 11.4%).

The hydrolysis of the formates (20) and (21) yielded 4-oxo-5β-cholestan-5-ol (22) in 50 and 98% yield, respectively, m.p. 173—175 °C (from methanol), $[\alpha]_D$ +8° (*c* 0.20) (lit.,[10c] m.p. 169—170 °C, $[\alpha]_D$ +15°); *m/z* 402 (7%, M^+), 356 (51%), and 332 (100%); $\nu_{max.}$ (KBr) 3 520 and 1 695 cm^{-1}; δ(CCl_4) 0.99 (3 H, s, 10-Me), 0.86 (6 H, d, *J* 6 Hz, 25-Me_2), and 0.63 (3 H, s, 13-Me) (Found: C, 80.65; H, 11.3. Calc. for $C_{27}H_{46}O_2$: C, 80.7; H, 11.4%). During the hydrolysis of the nitroimine (20) 30% of the 4-oxo-5α-cholestan-5-ol (19) was also obtained.

Reaction of Cholest-5-ene with Nitrous Acid and Boron Trifluoride–Ether Complex.—A solution in methylene chloride (100 ml) of cholest-5-ene (2.0 g), formic acid (20 ml), and boron trifluoride–ether (2 ml) was treated with sodium nitrite (2 g) as described for cholest-4-ene. After chromatography of the crude product (light petroleum–ethyl acetate 250 : 1 as eluant) were obtained 6-nitroimino-5α-cholestan-5-yl formate (14) (26%), 4-nitroimino-5α-cholestan-5-yl formate (17) (16%), 6-oxo-5α-cholestan-5-yl formate (15) (5%), 4-oxo-5β-cholestan-5-yl formate (21) (9%), and 4-oxo-5α-cholestan-5-yl formate (18) (12%). All these compounds are described as products of the reaction of cholest-4-ene with nitrous acid.

6β-*Nitroamino-5α-cholestan-5-ol* (27).—6-Nitroimino-5α-cholestan-5-yl formate (14) (0.73 g) in absolute ethanol (50 ml) was reduced with sodium borohydride (0.8 g) as described for the synthesis of 6β-nitroamino-5α-cholestane-3β,5-diol (26). Column chromatography (benzene–ethyl acetate 98 : 2 as eluant) gave 6β-*nitroamino-5α-cholestan-5-ol* (27) (0.5 g), non-crystalline; *m/z* 430 ($M^+ - H_2O$), 402 (74%, $M^+ - NO_2$), 386 (82%, $M^+ - NH_2NO_2$), 384 (100%, $M^+ - H_2O - NO_2$), and 368 (73%, $M^+ - NH_2NO_2 - H_2O$); $\nu_{max.}$ ($CHCl_3$) 3 600, 3 400, and 1 580 cm^{-1}; δ 8.7 (1 H, m, $W_{\frac{1}{2}}$ 27 Hz, NH), 4.20 (1 H, m, $W_{\frac{1}{2}}$ 9 Hz, 6α-H), 1.08 (3 H, s, 10-Me), 0.86 (6 H, d, *J* 6 Hz, 25-Me_2), and 0.68 (3 H, s, 13-Me) (Found: C, 72.35; H, 10.5; N, 6.1. $C_{27}H_{48}N_2O_3$ requires C, 72.3; H, 10.8; N, 6.25%).

4β-*Nitroamino-5α-cholestan-5-ol* (30).—4-Nitroimino-5α-cholestan-5-yl formate (30) (0.7 g) was reduced with sodium borohydride (0.7 g) in ethanol (50 ml) as already described for the preparation of the 6β-nitroamine (27). Column chromatography (benzene–ethyl acetate 98 : 2) yielded 4β-*nitroamino-5α-cholestan-5-ol* (30) (0.52 g) which crystallized from methanol, m.p. 180—181 °C, $[\alpha]_D$ +71° (*c* 0.06); *m/z* 430 (5%, $M^+ - H_2O$), 402 (10%, $M^+ - NO_2$), 386 (100%, $M^+ - NH_2NO_2$), and 384 (30%, $M^+ - H_2O - NO_2$); $\nu_{max.}$ ($CHCl_3$) 3 410 and 1 580 cm^{-1}; δ 8.5 (1 H, m, $W_{\frac{1}{2}}$ 30 Hz, NH), 4.20 (1 H, m, $W_{\frac{1}{2}}$ 9 Hz, 4α-H), 1.02 (3 H, s, 10-Me), 0.86 (6 H, d, *J* 6 Hz, 25-Me_2), and 0.65 (3 H, s, 13-Me) (Found: C, 72.2; H, 11.05; N, 6.0. $C_{27}H_{48}N_2O_3$ requires C, 72.3; H, 10.8; N, 6.25%).

6-*Nitroimino-5α-cholestan-3β-yl Acetate* (12).—To a solution of 6-oxo-5α-cholestan-3β-yl acetate (10) (2.2 g) in dry pyridine (50 ml), hydroxylamine hydrochloride (0.9 g) was added, and the solution was stirred at 90 °C for 3 h. After addition of water the mixture was extracted with chloroform. Usual work-up gave the oxime (11) (2.3 g), which was used without purification in the next reaction. To the oxime (11) (2.3 g), dissolved in methylene chloride (40 ml) containing solid sodium nitrite (2.44 g), a mixture of acetic acid (2 ml) and methylene chloride (10 ml) was added dropwise at 0 °C during 2 h. The mixture was worked up as usual giving 6-nitroimino-5α-cholestan-3β-yl acetate (12) (1.8 g) which could not be crystallized because rapid hydrolysis to the starting ketone (10) took place in solution. Notwithstanding, some spectroscopic data were obtained: $\nu_{max.}$

($CHCl_3$) 1 720, 1 625, 1 560, and 1 320 cm^{-1}; δ 4.68 (1 H, m, $W_{\frac{1}{2}}$ 24 Hz, 3α-H), 2.02 (3 H, s, 3β-OAc), 0.87 (6 H, d, *J* 6 Hz, 25-Me_2), 0.76 (3 H, s, 10-Me), and 0.66 (3 H, s, 13-Me).

6β-*Nitroamino*-5α-*cholestan*-3β-*yl Acetate* (32).[6a]—6-Nitroimino-5α-cholestan-3β-yl acetate (12) (1.7 g) in ethanol (30 ml) was reduced with sodium borohydride (2 g) as for the preparation of 6β-nitroamino-5α-cholestane-3β,5-diol (26). Column chromatography (benzene–ethyl acetate 9 : 1 as eluant) of the residue yielded 6β-*nitroamino*-5α-*cholestan*-3β-*yl acetate* (32) (1.18 g) which crystallized from benzene–ethanol, m.p. 194—196 °C, $[\alpha]_D$ −42° (*c* 0.29); *m/z* 444 (55%, $M^+ - NO_2$), 428 (25%, $M^+ - NH_2NO_2$), 384 (40%, $M^+ - NO_2 - AcOH$), and 368 (100%, $M^+ - NH_2NO_2 - AcOH$); $\nu_{max.}$ ($CHCl_3$) 3 400, 1 720, 1 570, and 1 330 cm^{-1}; δ 8.5 (1 H, d, *J* 7 Hz, NH), 4.72 (1 H, m, $W_{\frac{1}{2}}$ 20 Hz, 3α-H), 4.34 (1 H, m, $W_{\frac{1}{2}}$ 9 Hz, 6α-H), 2.04 (3 H, s, OAc), 1.00 (3 H, s, 10-Me), 0.87 (6 H, d, *J* 6 Hz, 25-Me_2), and 0.70 (3 H, s, 13-Me) (Found: C, 70.7; H, 10.35; N, 5.5. $C_{29}H_{50}N_2O_4$ requires C, 71.0; H, 10.25; N, 5.7%).

7-*Nitroiminocholest*-5-*en*-3β-*yl Acetate* (25).—A solution of 7-oxocholest-5-en-3β-yl acetate (23) (2.6 g) and hydroxylamine hydrochloride (2.2 g) in pyridine (75 ml) was treated as indicated for 6-oxo-5α-cholestan-3β-yl acetate (10), yielding the oxime (24) (2.5 g), $\nu_{max.}$ ($CHCl_3$) 3 580, 1 720, and 1 635 cm^{-1}; δ 6.61 (1 H, s, $W_{\frac{1}{2}}$ 3 Hz, H-6), 4.70 (1 H, m, $W_{\frac{1}{2}}$ 20 Hz, 3α-H), 2.05 (3 H, s, OAc), 1.13 (3 H, s, 10-Me), 0.87 (6 H, d, *J* 6 Hz, 25-Me_2), and 0.70 (3 H, s, 13-Me). The oxime (24) (2.4 g) in methylene chloride (300 ml) and acetic acid (15 ml) was treated as in the preparation of the 6-nitroimine (12). Column chromatography (n-hexane–ethyl acetate 25 : 2) yielded 7-*nitroiminocholest*-5-*en*-3β-*yl acetate* (25) (2.1 g), m.p. 158 °C (n-hexane), $[\alpha]_D$ −168° (*c* 0.26); *m/z* 440 (8%, $M^+ - NO_2$), 396 (24%), 380 (100%, $M^+ - NO_2 - AcOH$), and 368 (70%); $\lambda_{max.}$ (EtOH) 244 nm (ε 7 400); $\nu_{max.}$ ($CHCl_3$) 1 720, 1 630, 1 550, and 1 310 cm^{-1}; δ_H 5.82 (1 H, s, 6-H), 4.70 (1 H, m, $W_{\frac{1}{2}}$ 20 Hz, 3α-H), 2.05 (3 H, s, OAc), 1.19 (3 H, s, 10-Me), 0.87 (6 H, d, *J* 6 Hz, 25-Me_2), and 0.71 (3 H, s, 13-Me); δ_C ($CDCl_3$; Me_4Si standard) 170.5 (*C*OCH_3), 170.0 (7-C), 164.7 (5-C), 114.7 (6-C), 72.0 (3-C), 54.7 (17-C), 49.8 (14-C), 48.9 (9-C), 43.3 (13-C), 39.5, 39.4, 38.9, 38.4, 38.2, 36.2, 35.9, 35.6, 28.3, 28.0, 27.8, 27.2, 26.7, 23.8, 22.8 (27-C), 22.6 (26-C), 21.1 (11-C), 20.9 (CO-*C*H_3), 18.9 (21-C), 17.5 (19-C), and 12.1 (18-C) (Found: C, 71.7; H, 9.7; N, 5.6. $C_{29}H_{46}N_2O_4$ requires C, 71.55; H, 9.55; N, 5.75%).

Reduction of 7-*Nitroiminocholest*-5-*en*-3β-*yl Acetate* (25).—A solution of 7-nitroiminocholest-5-en-3β-yl acetate (25) in ethanol (150 ml) was treated with sodium borohydride (0.6 g) as for the preparation of 6β-nitroamino-5α-cholestane-3β,5-diol (26). Column chromatography of the residue (n-hexane–ethyl acetate 20 : 1 as eluant) yielded 7α-*nitroaminocholest*-5-*en*-3β-*yl acetate* (38) (0.35 g) and 7β-*nitroaminocholest*-5-*en*-3β-*yl acetate* (36) (0.30 g).

The 7α-nitroamine (38) crystallized from n-hexane; m.p. 178 °C; $[\alpha]_D$ −228° (*c* 0.28); *m/z* 444 (5%), 442 (5%, $M^+ - NO_2$), 426 (6%, $M^+ - NH_2NO_2$), 398 (12%), 384 (100%), 382 (70%, $M^+ - NO_2 - AcOH$), and 366 (25%, $M^+ - NO_2NH_2 - AcOH$); $\nu_{max.}$ ($CHCl_3$) 3 360, 1 720, 1 565, and 1 335 cm^{-1}; δ 9.16 (1 H, m, $W_{\frac{1}{2}}$ 13 Hz, NH), 5.57 (1 H, d, *J* 5 Hz, 6-H), 4.65 (2 H, m, $W_{\frac{1}{2}}$ 23 Hz, 3α-H, 7β-H), 2.06 (3 H, s, OAc), 1.04 (3 H, s, 10-Me), 0.91 (3 H, d, *J* 6 Hz, 20-Me), 0.86 (6 H, d, *J* 6 Hz, 25-Me_2), and 0.69 (3 H, s, 13-Me) (Found: C, 71.15; H, 10.2; N, 5.75. $C_{29}H_{48}N_2O_4$ requires C, 71.25; H, 9.9; N, 5.75%).

The 7β-nitroamine (36) crystallized from n-hexane; m.p. 134 °C, $[\alpha]_D$ +90° (*c* 0.19); *m/z* 444 (4%), 442 (7%, $M^+ - NO_2$), 426 (4%, $M^+ - NH_2NO_2$), 384 (100%), 382 (62%, $M^+ - NO_2 - AcOH$), and 366 (18%, $M^+ - NH_2NO_2 - AcOH$); $\nu_{max.}$ ($CHCl_3$) 3 380, 1 720, 1 570, and 1 320 cm^{-1}; δ 8.78 (1 H, m, $W_{\frac{1}{2}}$ 12 Hz, NH), 5.30 (1 H, br, s, $W_{\frac{1}{2}}$ 5 Hz, 6-H), 4.69 (1 H, m, $W_{\frac{1}{2}}$ 20 Hz, 3α-H), 4.43 (1 H, m, $W_{\frac{1}{2}}$ 13 Hz, 7α-H), 2.03 (3 H, s, OAc), 1.04 (3 H, s, 10-Me), 0.91 (3 H, d, *J* 6 Hz, 20-Me), 0.86 (6 H, d, *J* 6 Hz, 25-Me_2), and 0.73 (3 H, s, 13-Me) (Found: C, 71.55; H, 10.0; N, 5.6. $C_{29}H_{48}N_2O_4$ requires C, 71.25; H, 9.9; N, 5.75%).

General Procedure for Denitroamination of Steroid Nitroamines.—To a solution of the steroid nitroamine (1 mmol) in pyridine (30 ml), acetic anhydride (6 ml) was added and the mixture was kept at room temperature overnight. After addition of ice–water and solid sodium hydrogencarbonate, the products were extracted with diethyl ether. The organic layer was washed with aq. HCl, saturated $NaHCO_3$, and water, dried (Na_2SO_4), and evaporated under vacuum.

(i) 6β-*Nitroamino*-5α-*cholestane*-3β,5-*diol* (26). The nitroamine (26) (0.13 g) gave a product that was purified by column chromatography (benzene–ethyl acetate 95 : 5) yielding 5α,6α-epoxycholestan-3β-yl acetate (28) (0.09 g, 82%), which was recrystallized from methanol; m.p. 100—102 °C, $[\alpha]_D$ −43° (*c* 0.21) (lit.,[14] m.p. 101—103 °C, $[\alpha]_D$ −46°), identical with an authentic specimen.

(ii) 6β-*Nitroamino*-5α-*cholestan*-5-*ol* (27). The nitroamine (27) (0.2 g) gave a solid which by column chromatography (benzene–n-hexane 9 : 1) furnished 5α,6α-epoxycholestane (29) (0.12 g, 71%), m.p. 78 °C (MeOH), $[\alpha]_D$ −56° (*c* 0.23) (lit., [15] m.p. 74—75 °C, $[\alpha]_D$ −56°); *m/z* 380 (M^+); δ 2.87 (1 H, d, *J* 4 Hz, 6β-H), 1.05 (3 H, s, 10-Me), 0.87 (6 H, d, *J* 6 Hz, 25-Me_2), and 0.62, (3 H, s, 13-Me), identical with an authentic sample.

(iii) 4β-*Nitroamino*-5α-*cholestan*-5-*ol* (30). The nitroamine (30) (0.15 g) yielded a crude compound which was purified by column chromatography (benzene–n-hexane 9 : 1). Recrystallization from methanol afforded 4α,5α-epoxycholestane (31) (0.09 g, 71%), m.p. 100—102 °C, $[\alpha]_D$ +69° (*c* 0.23) (lit.,[15b,16] m.p. 101—102 °C, $[\alpha]_D$ +71°); *m/z* 386 (M^+); δ 2.91 (1 H, m, $W_{\frac{1}{2}}$ 6 Hz, 4β-H), 1.06 (3 H, s, 10-Me), 0.87 (6 H, d, *J* 6 Hz, 25-Me_2), and 0.69 (3 H, s, 13-Me), identical with a sample obtained from cholest-4-ene by treatment with *m*-chloroperbenzoic acid.

(iv) 6β-*Nitroamino*-5α-*cholestan*-3β-*yl acetate* (32). The nitroamine (32) (0.25 g) gave a residue which was chromatographed on a column of silica gel containing 20% $AgNO_3$ (n-hexane–ethyl acetate 99 : 1 as eluant) to yield an unresolved mixture (0.16 g) of cholest-4-en-3β-yl acetate (33) and cholest-5-en-3β-yl acetate (34) in an estimated ratio of 3 : 7 (^1H n.m.r.), and cholest-6-en-3β-yl acetate (35) (0.03 g), m.p. 103—105 °C (MeOH), $[\alpha]_D$ −89° (*c* 0.25) (lit.,[17] m.p. 104—106 °C, $[\alpha]_D$ −88°); δ 5.57, 5.46, 5.32, 5.21 (2 H, 6-H, 7-H), 2.04 (3 H, s, OAc), 0.88 (6 H, d, *J* 6 Hz, 25-Me_2), 0.81 (3 H, s, 10-Me), and 0.70 (3 H, s, 13-Me).

(v) 7β-*Nitroaminocholest*-5-*en*-3β-*yl acetate* (36). The nitroamine (36) (0.1 g) gave, after chromatography on silica gel containing 20% $AgNO_3$ (n-hexane–ethyl acetate 96 : 4), cholest-5-ene-3β,7β-diol diacetate (37) (0.08 g), m.p. 106—109 °C (MeOH), $[\alpha]_D$ +54° (*c* 0.30) (lit.,[18] m.p. 108—110 °C, $[\alpha]_D$ + 52°); δ 5.27 (1 H, m, $W_{\frac{1}{2}}$ 6 Hz, 6-H), 5.06 (1 H, m, $W_{\frac{1}{2}}$ 14 Hz, 7α-H), 4.64 (1 H, m, $W_{\frac{1}{2}}$ 30 Hz, 3α-H), 2.03 (6 H, s, OAc), 1.09 (3 H, s, 10-Me), 0.87 (6 H, d, *J* 6 Hz, 25-Me_2), and 0.70 (3 H, s, 13-Me) (Found: C, 76.4; H, 10.2. Calc. for $C_{31}H_{50}O_4$: C, 76.5; H, 10.35%); and cholest-5-ene-3β,7α-diol diacetate (39) (0.012 g), m.p. 120—122 °C (ace-

tone), $[\alpha]_D$ −175° (*c* 0.16) (lit.,[18] m.p. 123—124 °C, $[\alpha]_D$ −174°); δ 5.58 (1 H, d, *J* 5 Hz, 6-H), 4.96 (1 H, m, $W_{\frac{1}{2}}$ 9 Hz, 7β-H), 4.65 (1 H, m, $W_{\frac{1}{2}}$ 30 Hz, 3α-H), 2.03 (3 H, s, OAc), 1.02 (3 H, s, 10-Me), 0.87 (6 H, d, *J* 6 Hz, 25-Me_2), and 0.68 (3 H, s, 13-Me) (Found: C, 76.65; H, 10.43. Calc. for $C_{31}H_{50}O_4$: C, 76.5; H, 10.35%).

(vi) 7α-*Nitroaminocholest-5-en-3β-yl acetate* (38). The nitroamine (38) (0.1 g) gave a solid which was purified by column chromatography (n-hexane–ethyl acetate 95 : 5) to afford cholest-5-ene-3β,7α-diol diacetate (39) (0.09 g), identical with the previously described sample.

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