Steroidal *N*-Nitroamines. Part 3.[1] Pyrolytic Denitroamination of *N*-Nitroamino-adamantane and -bornane, and of Several Steroidal *N*-Nitroamines

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The thermal decomposition of several nitroamines has been investigated. The axial nitroamines 6β-nitroamino-5α-cholestan-3β-yl acetate (1) and 23*R*-nitroamino-(20*S*,22*S*,25*S*)-5β-spirostan-3β-yl acetate (8) gave exclusively nitrogen-free olefins. The *trans*-diaxial α-hydroxy nitroamines (2) and (3) afforded the 5α- and 4α-oxirane (6) and (7), and small amounts of the corresponding *trans*-diols (4) and (5). The 7β- and 7α-nitroaminocholest-5-en-3β-yl acetate (10) and (11) gave 7-oxocholesteryl acetate (14) and a mixture of the 7β- and 7α-alcohol (12) and (13) with 50 and 33% inversion of configuration, respectively. The oxidation product adamantanone (16) was produced together with adamantan-2-ol (20) in the pyrolysis of 2-nitroaminoadamantane (19). Carbon–carbon rearrangement was observed in the case of *exo*-2-nitroaminobornane (22) and 20β-nitroaminopregn-5-en-3β-yl acetate (25). The nitroamine (25) yielded the 3-*o*-acetyl derivatives of pregna-5,20-dien-3β-ol, (29), pregna-5,17(20)(*E*)-dien-3β-ol, (30), 3β-hydroxypregn-5-en-20-one, (28), 17α-methyl-D-homoandrost-5-ene-3β,17aβ-diol, (31), and a mixture of pregn-5-ene-3β,20-diols (26) and (27). Camphene (23) and tricyclene (24) was obtained from *exo*-2-nitroaminobornane (22). Mechanisms for the formation of these products are discussed.

We have recently described the synthesis of various steroidal nitroamines as well as their denitroamination reactions with acetic anhydride and pyridine.[1,2] Nitrogen-free products were obtained in all cases and their structures are consistent with the involvement of an N_2O-separated ion-pair mechanism.

The purpose of the study reported herein was to examine the pyrolytic behaviour of this functional group. Although the acid- and base-decomposition[3] of primary aliphatic *N*-nitroamines have been the objective of several works, not much has been done on the pyrolytic decomposition of these compounds. Franchimont *et al.*[4] found as early as 1896 that monoalkylnitroamines may decompose upon over-heating during distillation and they isolated methanol, *N,N*- and *N,O*-dimethylnitroamine, and nitrous oxide by thermal decomposition of methylnitroamine. By contrast, thermal rearrangement of primary and secondary aromatic nitroamines has been more extensively studied[5] due to the commercial interest of these compounds as explosives and propellants. Likewise, the pyrolysis of the closely related nitroimine group has been studied on camphor nitroimine.[6]

Results and Discussion

Preparation of the Substrates.—We have previously reported the synthesis of the steroidal nitroamines 6β-nitroamino-5α-cholestan-3β-yl acetate (1),[2] 6β-nitroamino-5α-cholestan-5-ol (2),[2] 4β-nitroamino-5α-cholestan-5-ol (3),[2] 23*R*-nitroamino-(20*S*,22*S*,25*S*)-5β-spirostan-3β-yl acetate (8),[1] 7β- and 7α-nitroaminocholest-5-en-3β-yl acetates (10)[2] and (11)[2] and 20β-nitroaminopregn-5-en-3β-yl acetate (25).[1,†]

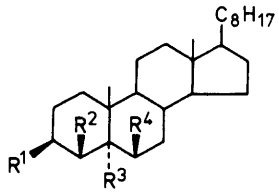
The adamantanone nitroimine (18) was prepared by the action of sodium nitrite in methylene dichloride–acetic acid on adamantanone oxime (17). The i.r. spectrum of the crude reaction showed a mixture of the nitroimine (18) [1 630 (C=N), and 1 560 and 1 320 cm^{-1} (NO_2)][7] and the starting ketone. The nitroimine (18) could not be purified since it is hydrolysed easily to the ketone (16). Sodium borohydride reduction[7] of the reaction mixture leads, after purification by chromatography, to 2-nitroaminoadamantane, (19), which exhibits in its i.r. spectrum characteristic absorptions for the nitroamino group[7] at 3 380 and 3 260 (NH), and 1 570 and 1 320 cm^{-1} (NO_2); in the ^1H n.m.r. spectrum the deuterium-oxide-exchangeable amine proton appears as a broad multiplet at δ 9.3 ($w_{\frac{1}{2}}$ 40 Hz) and the 2-H as a multiplet at δ 4.24 ($w_{\frac{1}{2}}$ 10 Hz).

The *exo*-2-nitroaminobornane (22) was synthesized by sodium borohydride reduction of camphor nitroimine (21).[8] The nitroamine (22) shows i.r. absorptions at 3 400 and 3 280 (NH), and 1 575 and 1 325 cm^{-1} (NO_2) and the mass spectrum confirms the presence of the nitroamine function (fragments corresponding to $M^+ - NO_2$ and $M^+ - NH_2NO_2$ at *m/z* 152 and 136, respectively). The *exo*-stereochemistry of the 2-nitroamine group is assigned on the basis of the shape of the 2-H signal in its ^1H n.m.r. spectrum, identical with the 2-H signal showed by isoborneol (bornan-2-ol).[9]

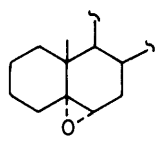
Pyrolysis of the Nitroamines.—The pyrolytic reactions were performed by heating the neat nitroamine in argon under the conditions specified in the Table. The axial nitroamines (1) and (8) gave exclusively cholesteryl acetate (15) and 23,24-dehydrosarsasapogenin acetate (9), respectively, by β-hydrogen elimination. Identical results were obtained upon treatment of these nitroamines with acetic anhydride–pyridine.[1,2] The pyrolysis of the *trans*-diaxial α-hydroxy nitroamines (2) and (3) led predominantly to the oxiranes (6) and (7), respectively, following an intramolecular substitution pathway. Also, minor amounts of the diols (4) and (5) were produced (with retention of configuration) by intramolecular substitution by the hydroxyl radical. The compounds obtained in these pyrolytic reactions can be satisfactorily rationalized in terms of a mechanism through an N_2O-separated radical pair (Scheme, path a), similar to that proposed for the denitroamination with acetic anhydride and pyridine.[1,2]

Thermal decomposition of the allylic nitroamines (10) and (11) gave a mixture of the epimeric alcohols (12) and (13), and the α,β-unsaturated ketone 7-oxocholesteryl acetate (14). The rates of inversion and retention for the substitution products (see Table) are slightly different from those observed for the denitroamination of these nitroamines with acetic anhydride–pyridine,[2] where total retention of configuration

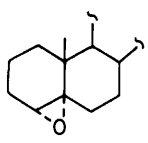
† 20*R*-Stereochemistry is assumed for this compound—see ref. 1, p. 298 (footnote *).



(1) R^1 = OAc, R^2 = R^3 = H, R^4 = $NHNO_2$
(2) R^1 = R^2 = H, R^3 = OH, R^4 = $NHNO_2$
(3) R^1 = R^4 = H, R^2 = $NHNO_2$, R^3 = OH
(4) R^1 = R^2 = H, R^3 = R^4 = OH,
(5) R^1 = R^4 = H, R^2 = R^3 = OH,



(6)



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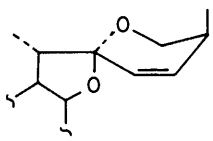

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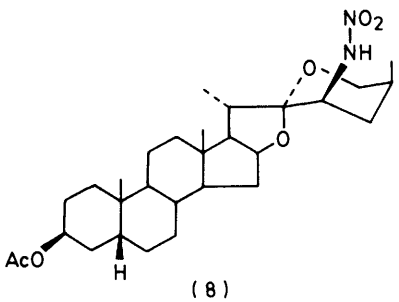

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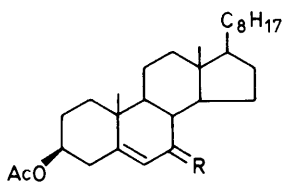
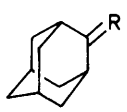


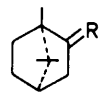
(10) R = α-H, β-$NHNO_2$
(11) R = α-$NHNO_2$, β-H
(12) R = α-H, β-OH
(13) R = α-OH, β-H
(14) R = O
(15) $R = H_2$



(16) R = O
(17) R = NOH
(18) R = NNO_2
(19) R = H, $NHNO_2$
(20) R = H, OH

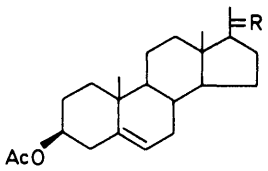
C_8H_{17} = -CH(CH_3)[CH_2]$_3$CH(CH_3)$_2$

was found for the pseudoaxial nitroamine (11) and only 14% of inversion for the pseudoequatorial nitroamine (10). The formation of the ketone (14) was unexpected and it can be explained in terms of a redox process as we propose in the Scheme (path b). The hydrogen on the carbon atom is transferred directly to the *aci*-nitro group through an intramolecular cyclic transition state * to give the intermediate (A); subsequent thermal [1,3]sigmatropic rearrangement leads to the *aci*-nitrosoamine (B) which undergoes nitrogen extrusion to give ketone (C). The ready accessibility of the equatorial



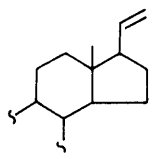
(21) R = NNO_2
(22) R = *exo*-$NHNO_2$, *endo*-H

(23)



(25) R = α-H, β-$NHNO_2$
(26) R = α-H, β-OH
(27) R = α-OH, β-H
(28) R = O

(24)



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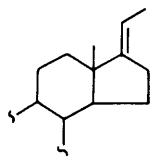

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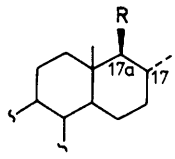


(31) R = OH
(32) R = OAc

hydrogen in the axial nitroamine, necessary to form the cyclic intermediate, is in agreement with the larger amount of ketone (14) produced during the pyrolysis of the axial isomer (11) (40%) as compared with the equatorial one (10) (22%). With the aim of studying the thermal decomposition of nitroamines when the highly favoured β-hydrogen elimination is structurally forbidden, we prepared 2-nitroaminoadamantane (19) which, upon pyrolysis, gave exclusively adamantan-2-ol (20) and adamantanone (16). The formation of adamantanone indicates that the oxidation process is not exclusive of allylic systems, where stabilized α,β-unsaturated ketones are obtained. Furthermore, as 2,2′-biadamantane was not detected in the reaction mixture, the involvement of free radicals is not significant.†

The carbon–carbon rearrangements produced in the denitroamination reaction of some nitroamines with acetic anhydride–pyridine [1] were also observed in the nitroamine pyrolyses. Thus, the 20β-nitroaminopregn-5-en-3β-yl acetate (25) (20*R*-stereochemistry) gave 17aβ-hydroxy-17α-methyl-D-homoandrost-5-en-3β-yl acetate (31), and the pyrolysis of *exo*-2-nitroaminobornane (22) leads exclusively to the rearranged compound camphene (23), and tricyclene (24) as the minor component. Likewise, during nitrous acid deamination of *exo*-2-bornylamine, camphane-skeleton compounds are predominantly produced.[10] The pyrolysis of compound (25) afforded, besides the D-homo compound (31), elimination- (29) and (30), substitution- (26) and (27), and oxidation-products (28). It should be pointed out that substitution at C-20 takes place with 35% inversion of configuration, by contrast with the complete retention of configuration observed during the denitroamination with acetic anhydride and pyridine.[1]

In summary, we have studied the thermal decomposition of

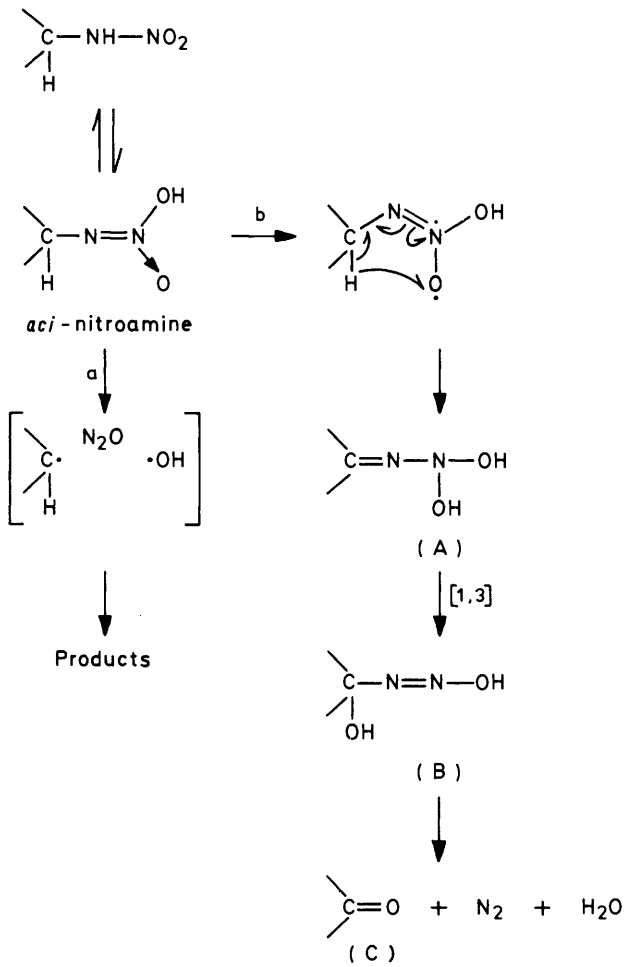
* An analogous cyclic transition state has been postulated and is currently accepted for the chromic acid oxidation of alcohols (D. N. Kirk and M. P. Hartshorn, 'Steroid Reaction Mechanisms,' Elsevier, Amsterdam, 1968, p. 314; R. Stewart, 'Oxidation Mechanisms,' W. A. Benjamin, New York, 1964, p. 37).

† In contrast, 2,2′-biadamantane is formed, through a free-radical pathway, during the pyrolytic decomposition of 2-dimethylaminoadamantane *N*-oxide (K. H. Overton and E. Suárez, unpublished results).

Table. *N*-Nitroamine pyrolysis

Compound	Conditions: temperature (°C); time (h)	Products and yields (%) Elimination	Oxidation	Substitution	Rearrangement	Starting material
(1) [a]	170; 3	(15) [a] 71	—	—	—	—
(2) [a]	200; 0.5	—	—	(6) [a] 68; (4) 13	—	—
(3) [a]	185; 0.5	—	—	(7) [a] 72; (5) 9	—	—
(8) [b]	165; 3	(9) [b] 55	—	—	—	(8) [b] 10
(10) [a]	160; 1	—	(14) 22	(12) 22; (13) 22	—	(10) [a] 19
(11) [a]	160; 1	—	(14) 40	(12) 8; (13) 24	—	(11) [a] 12
(19)	160; 1	—	(16) 33	(20) 43	—	(19) 12
(21)	130; 60	—	—	—	(23) 81; (24) 9	—
(25) [b]	195; 1	(29) [b] 28; (30) [b] 3	(28) 10	(26) 25; (27) 14	(31) 15	—

[a] Product described in ref. 2. [b] Product described in ref. 1.



Scheme.

several *N*-nitroamines and we have rationalized the products on the basis of a mechanism that involves an N_2O-separated radical pair. Moreover, we found that the results are generally comparable to those observed for the acetic anhydride–pyridine denitroamination. The main differences are, on the one hand, the formation of oxidized products, and on the other the minor retention of configuration in the substitution products, possibly due to a lesser effectiveness of the diradical cage.

Experimental

M.p.s were determined with a Kofler hot-stage apparatus and are uncorrected. Optical rotations were measured for solutions in $CHCl_3$. I.r. spectra were taken on a Perkin-Elmer 257 instrument, and ^1H n.m.r. spectra were recorded in $CDCl_3$ with a Perkin-Elmer R-12B (60 MHz) and a Perkin-Elmer R-32 (90 MHz) spectrometer. G.l.c. was performed with a Hewlett-Packard 5710A instrument. T.l.c. was run 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–water (1 : 20 : 4), vanillin (1 g)–H_2SO_4 (160 ml)–EtOH (40 ml), or I_2.

The steroidal nitroamines 6β-nitroamino-5α-cholestan-3β-yl acetate (1), 6β-nitroamino-5α-cholestan-5-ol (2), 4β-nitroamino-5α-cholestan-5-ol (3), 23*R*-nitroamino-(20*S*,22*S*,25*S*)-5β-spirostan-3β-yl acetate (8), 7β-nitroaminocholest-5-en-3β-yl acetate (10), 7α-nitroaminocholest-5-en-3β-yl acetate (11), and 20*R*-nitroaminopregn-5-en-3β-yl acetate (25) * have been previously described.[1,2]

2-Nitroaminoadamantane (19).—To a solution of adamantanone (16) (3 g) in pyridine (60 ml) was added hydroxylamine hydrochloride (2.1 g) and the mixture was stirred at 90 °C for 3 h. Usual work-up gave the oxime (17) (3.5 g), which was used without purification in the next step.

To a solution of the oxime (17) (3.5 g) in methylene dichloride (175 ml) containing sodium nitrite (9.6 g) was added dropwise a mixture of acetic acid (6.9 ml) and methylene dichloride (175 ml) at room temperature during 2.5 h. The mixture was then stirred at room temperature for 1.5 h and worked up as usual to give a 2 : 1 mixture (3.4 g) of *2-nitroiminoadamantane* (18) and adamantanone (16) which could not be separated by chromatography due to the easy hydrolysis of the nitroimine to the ketone.

This mixture (3.4 g) of 2-nitroiminoadamantane (18) and adamantanone (16), in absolute ethanol (400 ml), was reduced with sodium borohydride (2 g) for 1 h at room temperature. Usual work-up gave a residue which was chromatographed [n-hexane–diethyl ether (7 : 3) as eluant] to yield adamantan-2-ol (20) (0.5 g) and *2-nitroaminoadamantane* (19) (1.9 g), purified by sublimation (100 °C at 0.1 mmHg), m.p. 104 °C (Found: C, 61.1; H, 8.3; N, 14.1. $C_{10}H_{16}N_2O_2$ requires C, 61.2; H, 8.2; N, 14.3%); $\nu_{max.}$ ($CHCl_3$) 3 380, 3 260 (NH), 1 570, and 1 320 cm^{-1}(NO_2); δ 9.3 (1 H, m, $w_{\frac{1}{2}}$ 40 Hz, NH), 4.24 (1 H, m, $w_{\frac{1}{2}}$ 10 Hz, 2-H), 2.13 (2 H, m, $w_{\frac{1}{2}}$ 18 Hz, 1-H and 3-H), and 1.85 (12 H, m, $w_{\frac{1}{2}}$ 18 Hz).

* 20*R*-stereochemistry assumed—see ref. 1, p. 298 (footnote *).

exo-2-*Nitroaminobornane* (22).—To a solution of 2-nitroiminobornane (21) [8] (2 g) in diethyl ether (30 ml) was added lithium aluminium hydride (0.5 g) and the mixture was refluxed for 2 h. Usual work-up yielded a residue which was crystallized from methanol to give *exo*-2-nitroaminobornane (22) (1.5 g), m.p. 81—83 °C (lit.,[8] 98—99° C); $[\alpha]_D$ −51° (*c* 0.3); *m/z* 152 (3%, $M^+ - NO_2$), 137 (1, $M^+ - NHNO_2$), 136 (1, $M^+ - NH_2NO_2$), 109 (12), 108 (18), 95 (60), 83 (40), and 81 (100); $\nu_{max.}$ ($CHCl_3$) 3 400 and 3 280 (NH), and 1 575 and 1 325 cm^{-1} (NO_2); δ 8.8 (1 H, m, $w_{\frac{1}{2}}$ 18 Hz, NH), 4.13 (1 H, m, $w_{\frac{1}{2}}$ 18 Hz, 2-H), and 0.96, 0.91, and 0.87 (together 9 H, 3 s, 1-Me and 7-Me_2).

Pyrolysis of Nitroamines.—General procedure. The pyrolyses were performed in a Büchi Kugelrohrofen under argon and without solvent. 2-Nitroaminoadamantane (19) and *exo*-2-nitroaminobornane (22) were pyrolysed in a sealed tube under argon. The reaction conditions are specified in the Table and the products from the thermolysis were purified by dry-column chromatography on silica gel, silica gel containing 20% $AgNO_3$, or by preparative t.l.c. plates.

The compounds shown in the Table have been previously described by us in parts 1 and 2 of this series [1,2] except for adamantan-2-ol and adamantanone which were directly compared with authentic samples.

Camphene (23) and tricyclene (24) were identified and quantitatively analysed by gas chromatography [1/8 in × 6 ft; 2.5% SE-30 on Chromosorb G; column temperature programmed from 80 °C (previously maintained for 6 min) to 90 °C at 3 °C min^{-1}] using fenchone and camphor as internal standards. (The ^1H n.m.r. spectrum of this 8 : 2 mixture of camphene and tricyclene was identical with that recorded previously).*

5α-*Cholestane*-5,6β-*diol* (4). This had m.p. 118—120 °C (from MeOH) (lit.,[11] 119—121 °C); δ 3.53 (1 H, m, $w_{\frac{1}{2}}$ 6 Hz, 6-H), 1.15 (3 H, s, 10-Me), 0.85 (6 H, d, *J* 6 Hz, 25-Me_2), and 0.67 (3 H, s, 13-Me); identical with a sample obtained by acid-catalysed hydrolysis of 5α,6α-epoxycholestane (6).

5α-*Cholestane*-4β,5-*diol* (5). This had m.p. 170—172 °C (MeOH) (lit.,[12] 171—172 °C); δ 3.51 (1 H, m, $w_{\frac{1}{2}}$ 6 Hz, 4-H), 1.17 (3 H, s, 10-Me), 0.86 (6 H, d, *J* 6 Hz, 25-Me_2), and 0.67 (3 H, s, 13-Me); identical with a sample obtained by acid-catalysed hydrolysis of 4α,5α-epoxycholestane (7).

7β- *and* 7α-*Hydroxycholest*-5-*en*-3β-*yl* 3-*acetate* (12) *and* (13). These could not be separated by chromatography and exhibited n.m.r. signals at δ 5.64 (d, *J* 6 Hz, 6-H for 7α-ol), 5.32 (m, $w_{\frac{1}{2}}$ 6 Hz, 6-H for 7β-ol), 4.69 (m, $w_{\frac{1}{2}}$ 30 Hz, 3α-H), 3.86 (m, $w_{\frac{1}{2}}$ 15 Hz, 7β- and 7α-H), 2.03 (s, OAc), 1.07 [s, 10-Me in (12)], 1.01 [s, 10-Me in (13)], 0.87 (d, *J* 6 Hz, 25-Me_2), and 0.68 (s, 13-Me). Acetylation of the mixture and separation by column chromatography on silica gel containing 20% $AgNO_3$ [n-hexane–ethyl acetate (96 : 4) as eluant] gave the previously described diacetates.[2]

20R-*Hydroxypregn*-5-*en*-3β-*yl acetate* (26). This had m.p. 163.5—165.5 °C (from MeOH); $[\alpha]_D$ −74° (*c* 0.28) (lit.,[13] m.p. 164.5—165.5 °C; $[\alpha]_D$ −68°); *m/z* 300 (100%, M^+ − AcOH), 285 (20, M^+ − AcOH − Me), 282 (25, M^+ − AcOH − H_2O), 267 (16), and 255 (10); $\nu_{max.}$ (KBr) 3 550, 1 720, and 1 250 cm^{-1}; δ 5.39 (1 H, m, $w_{\frac{1}{2}}$ 10 Hz, 6-H), 4.60 (1 H, m, $w_{\frac{1}{2}}$ 27 Hz, 3α-H), 3.75 (1 H, m, $w_{\frac{1}{2}}$ 20 Hz, 20-H), 2.03 (3 H, s, OAc), 1.14 (3 H, d, *J* 6 Hz, 20-Me), 1.03 (3 H, s, 10-Me), and 0.77 (3 H, s, 13-Me).

20S-*Hydroxypregn*-5-*en*-3β-*yl acetate* (27). This had m.p. 139—141 °C (from MeOH); $[\alpha]_D$ −62° (*c* 0.21) (lit.,[13] m.p. 142—143 °C; $[\alpha]_D$ −56°); *m/z* 300 (100%, M^+ − AcOH), 285 (15, M^+ − AcOH − Me), 282 (25, M^+ − AcOH − H_2O), 267 (20), and 255 (10); $\nu_{max.}$ (KBr) 3 380, 1 725, and 1 240 cm^{-1}; δ 5.39 (1 H, m, $w_{\frac{1}{2}}$ 10 Hz, 6-H), 4.60 (1 H, m, $w_{\frac{1}{2}}$ 27 Hz, 3α-H), 3.72 (1 H, m, $w_{\frac{1}{2}}$ 20 Hz, 20-H), 2.03 (3 H, s, OAc), 1.23 (3 H, d, *J* 6 Hz, 20-Me), 1.03 (3 H, s, 10-Me), and 0.68 (3 H, s, 13-Me). The compounds (26) and (27) were directly compared with authentic samples obtained from 20-oxopregn-5-en-3β-yl acetate (28) by Raney nickel-catalysed hydrogen reduction.[14]

17αβ-Hydroxy-17α-methyl-D-homoandrost-5-en-3β-yl acetate (31) was acetylated with acetic anhydride in pyridine to give the previously described diacetate (32).[1]

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