Steroids. Part 21.[1] Photorearrangement of Steroidal Nitronate Salts and a *N*-Butyl Spiro-oxaziridine†

Graham J. Edge, Syed H. Imam, and Brian A. Marples*
Department of Chemistry, University of Technology, Loughborough, Leics. LE11 3TU

Irradiation, at 254 nm, of ethanol solutions of nitro-steroids in the presence of an excess of sodium ethoxide gave a range of products including hydroxamic acids, ketones, and alkenes possibly derived from the anions of the *N*-hydroxyoxaziridines. Alternatively, the ketones and hydroxamic acids may be derived from the anions of the hydroxy-nitroso compounds. The proportions of products depend on the ring size and stereochemistry and the photoreactions differ significantly from those observed for *N*-alkyl spiro-oxaziridines including a steroidal *N*-butyl spiro-oxaziridine.

The photochemical reactions of nitro compounds have been extensively investigated.[2] Until our preliminary work[3] on the photochemistry of the 17β-nitro-5α-androstane (**3**) there were no reports of the photochemistry of nitronate salts. Recently, similar results to our own were observed by another group[4] and this prompts us to report further details of our own findings in this area.

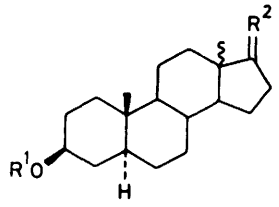
17-Nitro Compounds.—The 17β-nitro-5α-androstane (**3**),[5] its Δ^5-analogue (**10**),[6] and the 13α-derivative (**4**) were prepared from the corresponding oximes by sequential treatment with *N*-bromosuccinimide (NBS)–O_2 and $NaBH_4$.[6] The oxime (**2**) was available from the 13α-ketone (**5**)[7] which was prepared by hydrogenation of the Δ^5-13α-ketone (**11**) obtained by treatment of the oxime (**9**) with acetic anhydride and pyridine under reflux.[8]

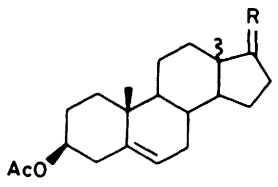
The photolysis of the 17β-nitro-5α-androstane (**3**) was carried out in ethanol containing an excess of NaOEt, first of all using a medium-pressure mercury lamp; however, cleaner reactions were observed using a low-pressure mercury lamp, having its principal emission at 254 nm, which is close to the absorption band of the nitronate salts (*ca.* 240 nm). Accordingly, all the photolyses were carried out under these conditions.

Crystallisation of the crude product from the photolysis of the 17β-nitro-5α-androstane (**3**) gave the hydroxamic acid (**12**) (55%) and chromatography of the mother-liquors gave a mixture (11%) ($\nu_{max.}$ 1 735 cm^{-1}) of the 13β- and 13α-17-ketones (**8**)[7] and (**7**)[7] (see ^1H n.m.r. data below) which were separated from the 17,18-cycloandrostane (**25**) (7%).[9] The hydroxamic acid (**12**) showed a characteristic i.r. spectrum ($\nu_{max.}$ 1 620 cm^{-1}) and was converted into the known lactam (**14**)[10] by reduction with Zn–CH_3CO_2H and subsequent acetylation. Conversion of the hydroxamic acid (**12**) into its *O*-methyl derivative (**15**), by treatment with NaH–MeI in dimethylformamide (DMF), and its diacetate (**16**), by treatment with acetic anhydride–pyridine, provided further characterisation. No evidence could be obtained for the presence of any regioisomer or the 13α-epimer (**13**) of the hydroxamic acid (**12**). This was confirmed by examination of the total lactam fraction obtained by reduction of the total crude photolysate with Zn–CH_3CO_2H; only the lactam (**14**) was isolated.

The photolysis of the 17β-nitroandrost-5-ene (**10**) similarly gave the hydroxamic acid (**22**) (65%) ($\nu_{max.}$ 1 610 cm^{-1}) which on acetylation gave the diacetate (**23**). Reduction with Zn–CH_3CO_2H of the crude photolysate from a further reaction and acetylation gave the known lactam (**24**).[10]

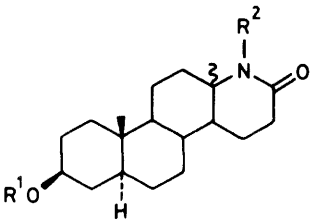
The photolysis of the 17β-nitro-5α,13α-androstane (**4**) gave a mixture which was purified by preparative t.l.c. to give some 17-ketone (55%) ($\nu_{max.}$ 1 730 cm^{-1}) which was shown by its ^1H n.m.r. spectrum[11] to be mainly the 13α-17-ketone (**7**)[7] [δ 0.93 (13α-Me) and 0.63 (10β-Me)] contaminated with a little 13β-17-ketone (**8**)[7] [(δ 0.80 (13β- and 10β-Me)]. The remaining major product (22%) was the hydroxamic acid (**13**) ($\nu_{max.}$ 1 610 cm^{-1}). In a further experiment, the crude photolysate was acetylated and subjected to preparative t.l.c. and gave the diacetate (**17**)

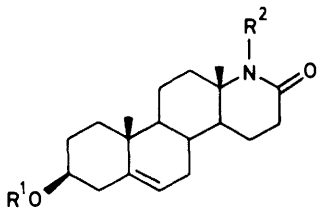




(**1**) R^1 = Ac, R^2 = NOH; 13β
(**2**) R^1 = Ac, R^2 = NOH; 13α
(**3**) R^1 = Ac, R^2 = β-NO_2,H; 13β
(**4**) R^1 = Ac, R^2 = NO_2,H; 13α
(**5**) R^1 = Ac, R^2 = O; 13α
(**6**) R^1 = Ac, R^2 = O; 13β
(**7**) R^1 = H, R^2 = O; 13α
(**8**) R^1 = H, R^2 = O; 13β

(**9**) R = NOH; 13β
(**10**) R = β-NO_2,H; 13β
(**11**) R = O; 13α

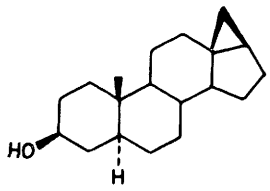




(**12**) R^1 = H, R^2 = OH; 13β
(**13**) R^1 = H, R^2 = OH; 13α
(**14**) R^1 = Ac, R^2 = H; 13β
(**15**) R^1 = H, R^2 = OMe; 13β
(**16**) R^1 = Ac, R^2 = OAc; 13β
(**17**) R^1 = Ac, R^2 = OAc; 13α
(**18**) R^1 = R^2 = H; 13β
(**19**) R^1 = THP, R^2 = H; 13β
(**20**) R^1 = THP, R^2 = Bu; 13β
(**21**) R^1 = Ac, R^2 = Bu; 13β

(**22**) R^1 = H, R^2 = OH
(**23**) R^1 = Ac, R^2 = OAc
(**24**) R^1 = Ac, R^2 = H

† Part of this work was presented at the Xth International Conference on Photochemistry, Iraklion, Crete, September 1981 (see abstract *J. Photochem.*, 1981, **17**, 97) and at the East Midlands Regional Symposium of the Perkin Division of the Royal Society of Chemistry, Leicester University, December 1983.



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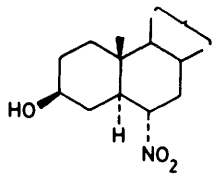

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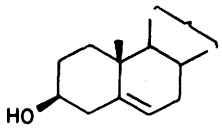

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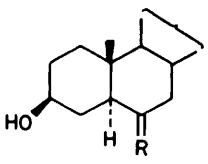
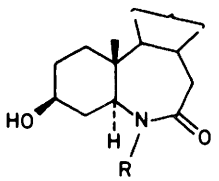
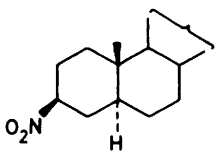


(28) R = O
(29) R = H_2



(30) R = OH
(31) R = H



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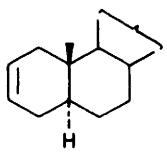

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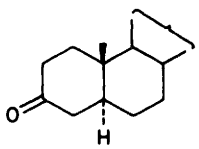


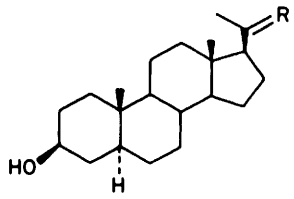
(34)

(27%) and two fractions which were identified as the 13α-17-ketone (**5**)[7] (22%) and a mixture of the 13α- and 13β-17-ketones (**5**) and (**6**)[7] (27%) by their ^{1}H n.m.r. spectra.[11]

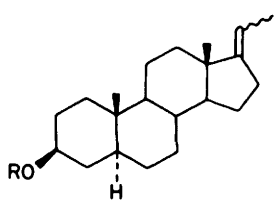
6α-Nitrocholestan-3β-ol (**26**).[12]—Preparative t.l.c. of the photolysate gave four major fractions which contained cholesterol (**27**) (18%), 3β-hydroxy-5α-cholestan-6-one (**28**) (22%),[13] and 3β-hydroxy-5α-cholestane (**29**) (17%).[14] It was necessary to rechromatograph the cholesterol-containing fraction (36%) on silver nitrate-impregnated silica to remove some impurity which was not identified. The fourth fraction (15%) was tentatively identified as the hydroxamic acid (**30**) having a typical[15] carbonyl absorption at $\nu_{max.}$ 1 660 cm^{-1}. The mass spectrum showed no molecular ion, but did show a peak at *m/z* 417 corresponding to the loss of an oxygen atom. Such fragmentations have previously been reported for seven-membered cyclic hydroxamic acids.[15] Full characterisation of this fraction, however, was not possible. Attempts to isolate the equivalent lactam (**31**) by chromatography of the Zn–CH_3CO_2H reduced crude photolysate failed.

3β-Nitro-5α-cholestane (**32**).[16]—Preparative t.l.c. of the crude photolysate gave 5α-cholest-2-ene (**33**) (22%)[17] and 5α-cholestan-3-one (**34**) (16%).[14] The remainder of the photolysate appeared to be polymeric.

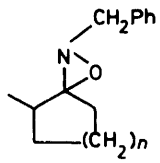
20β-Nitro-5α-pregnan-3β-ol (**36**).—Oxidation of the 20β-amine (**35**)[18] with MCPBA gave the 20β-nitro compound (**36**) which was photolysed under the usual conditions to afford,



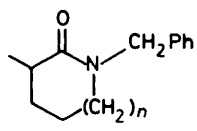
(35) R = β-NH_2, H
(36) R = β-NO_2, H
(37) R = O



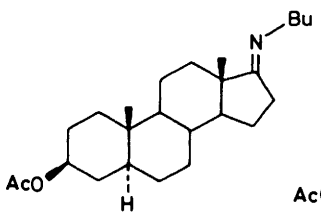
(38) R = H: *Z* and *E*
(39) R = Ac; *E*



(41) *n* = 1
(42) *n* = 2



(43) *n* = 1
(44) *n* = 2



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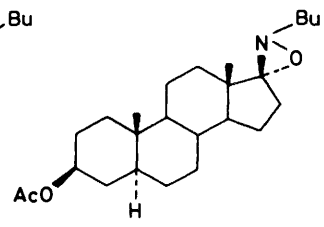

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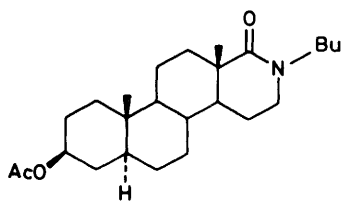


(47)

after preparative t.l.c., the 20-ketone (**37**) (22%)[19] and a mixture (35%) of the $\Delta^{17(20)}$-compounds (**38**). The major component, the (*E*)-isomer[20] (20%), was separated from the mixture by rechromatography on silver nitrate impregnated silica and was acetylated to give the acetoxy alkene (**39**).[21]

It is apparent that substantial conversion into hydroxamic acids occurs only in the photolyses of the 17-nitro 13β-compounds (**3**) and (**10**), and other reactions compete effectively in the remaining photolyses. In our preliminary communication[3] we suggested that an *N*-hydroxyoxaziridine sodium salt (**40**) (Scheme) could be intermediate in the photolysis of 17β-nitro 13β-compound (**3**). The photorearrangements of oxaziridines to amides are well known[22,23] and spiro-oxaziridines are proposed intermediates in the photo-Beckmann rearrangement of ketoximes.[24] Of particular relevance to our study is the observation[22] that on photorearrangement the spiro-oxaziridines (**41**) and (**42**) undergo ring expansion to the lactams (**43**) and (**44**) respectively by migration of the less substituted carbon atom. We were interested in the comparison between these systems and our own where only the more substituted carbon, C-13, migrates. It was also relevant to compare the photo-Beckmann rearrangement where little regioselectivity and stereoselectivity is observed for 17-

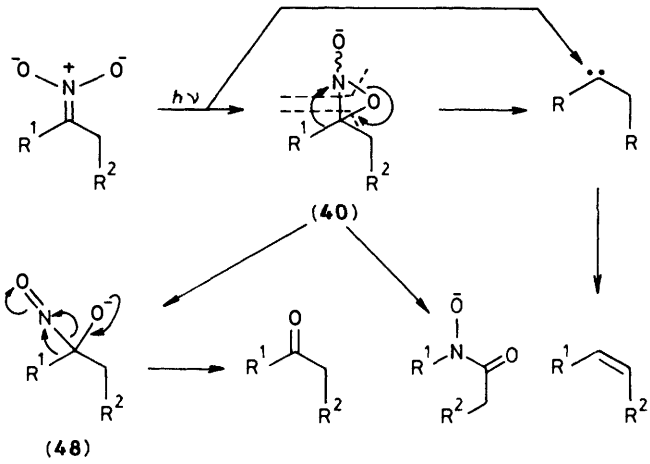
Table. ^{13}C N.m.r. data for the *N*-butyl spiro-oxaziridine (**45**)

Nucleus	δ/p.p.m. (6)*	(45)
C-1	36.75	36.85
C-2	27.73	27.5
C-3	73.28	73.7
C-4	34.35	34.06
C-5	44.62	44.72
C-6	28.44	28.48
C-7	32.05	31.44
C-8	35.0	35.48
C-9	54.36	54.23
C-10	35.55	35.65
C-11	20.57	20.28
C-12	30.79	30.51
C-13	47.41	42.32
C-14	51.29	51.22
C-15	21.72	23.18
C-16	35.0	25.53
C-17	212.3	96.0
C-18	13.68	13.94
C-19	11.99	12.19
N-Butyl group		
α-CH_2		56.75
β-CH_2		30.4
γ-CH_2		21.38
Me		14.71
OAc Group		
CO	169.66	170.69
Me	20.95	20.61

* Data for the 3β-hydroxy-5α-androstan-17-one are available: J. W. Blunt and J. B. Stothers, *Org. Magn. Reson.*, 1977, **9**, 439.

ketoximes.[24] Accordingly, we have examined the photolysis of the *N*-butyl spiro-oxaziridine (**46**) which was prepared by MCPBA oxidation, at *ca.* 5 °C in benzene–ethanol,[25] of the crude *N*-butylimine (**45**) which was available from the ketone (**6**)[7] by reaction with butylamine in the presence of toluene-*p*-sulphonic acid (PTSA).[26] The *N*-butylimine (**45**) was characterised by its ^1H n.m.r. [δ 3.2 (t, 2 H, N-C$H_2C_3H_7$)] and i.r. [$\nu_{max.}$ 1 675 cm^{-1} (C=N)] spectra. Its mass spectrum showed a molecular ion at *m/z* 387. Preparative t.l.c. of the crude *N*-butyl spiro-oxaziridine (**46**) gave material which showed a triplet at δ 2.7 (2 H, >C(O)–NC$H_2C_3H_7$) in the ^1H n.m.r. spectrum and a molecular ion at *m/z* 403.3101. The ^1H n.m.r. data for the *N*-butylimine (**45**) and the *N*-butyl spiro-oxaziridine (**46**) are consistent with the literature data on similar systems.[27] The stereochemistry of the *N*-butyl spiro-oxaziridine (**46**) was assigned, in part, from its ^{13}C n.m.r. spectrum by comparison with that of the ketone (**6**) (Table). A key difference is the chemical shift of the C-13 signal which is upfield in the *N*-butyl spiro-oxaziridine (**46**) relative to its position in the ketone (**6**) by 5.09 p.p.m. Such relatively small upfield shifts for the chemical shift of the carbon *anti* to the *N*-alkyl group in spiro-oxaziridines have previously been observed.[28] The upfield shift of the signal for the carbon *syn* to the *N*-alkyl group is usually considerably larger than that for the *anti* carbon, and although the signal for C-16 cannot be assigned unequivocally,* it is clear that the lowest possible assignment is at 25.53 p.p.m. Thus, the

* The assignments of the signals for C-15, C-16, and the γ-CH_2 of the *N*-butyl residue are tentative.



Scheme.

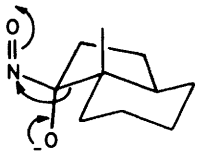
minimum upfield shift for the C-16 in converting the ketone (**6**) into the *N*-butyl spiro-oxaziridine (**46**) is 9.5 p.p.m. The α-configuration of the oxygen of the *N*-butyl spiro-oxaziridine (**46**) is assigned on the basis of the well known preferred α-face attack at C-17.

Photolysis of the *N*-butyl spiro-oxaziridine (**46**), in ethanol at 254 nm, and preparative t.l.c. of the crude product, gave the *N*-butyl lactam (**47**) (50%) and the ketone (**6**)[7] (25%). The *N*-butyl lactam (**47**) showed a band in the i.r. spectrum at 1 620 cm^{-1} ($CONR_2$) and a multiplet in the ^1H n.m.r. spectrum (δ 3.25, 4 H) which was assigned to the N–CH_2Pr and the N–CH_2 (C-16) moieties supporting structure (**46**) rather than the regioisomer (**21**). This assignment was confirmed by synthesis of the regioisomer (**21**) which was shown to be different from the *N*-butyl lactam (**47**). In particular, the ^1H n.m.r. spectrum showed two separate signals for the α-protons of the N–Bu group at δ 2.9 and 3.5 and a multiplet at δ 2.4 which was assigned to the C-16 methylene group. The non-equivalence of the α-protons of the N–Bu group may be due to some restriction of rotation around the N–CH_2 bond by steric interaction between the β-methylene group and the C-12 methylene group. The regioisomer (**21**) was prepared from the lactam (**18**) which was intially converted into the tetrahydropyranyl ether (**19**). Without purification, the tetrahydropyranyl ether (**19**) was *N*-butylated using NaH–DMF–BuI and the resultant *N*-butyl lactam (**20**) was deprotected and acetylated to afford the required *N*-butyl lactam (**21**) which was purified by t.l.c.

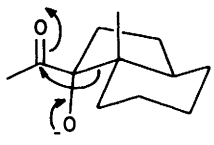
Discussion

The major products of photolysis of the nitronate anions appear to be hydroxamic acids, alkenes, and ketones. These may arise from a common intermediate *N*-hydroxyoxaziridine sodium salt (**40**) by three distinct pathways, as indicated in the Scheme. Except for the photolysis of the 20β-nitro compound (**36**), the intermediate (**40**) would be a spiro-oxaziridine derivative. The suggestion that alkenes arise from a carbene produced by elimination of nitrite ion is supported by the isolation of the 17,18-cycloandrostane (**25**)[9] in the photolysis of the 17β-nitro-5α-androstane (**3**). Similar carbene insertion has been observed in the reaction of tosylhydrazones of 17-ketones with strong base in an aprotic solvent.[9] There is no evidence that the 17,18-cycloandrostane (**25**) arises from the free 17β-nitro-5α-androstane (**3**) rather than its anion[4] since no 17,18-cycloandrostane was detected in the photolysate obtained in the absence of sodium ethoxide. The conversion of *N*-hydroxyoxaziridine sodium salts (**40**) into ketones requires

the elimination of hyponitrite ion. It has recently been suggested[4] that the *N*-hydroxyoxaziridine anions are not intermediates in the photolyses, but are extremely short lived species which collapse to the anions (**48**) (Scheme). It is apparent that ketones and hydroxamic acids could arise from such anions (**48**), but the conversion into carbenes may require the intermediacy of (**40**). It is, of course, possible that the carbenes may arise directly from the nitronate salt and that this is a competitive reaction with the formation of the *N*-hydroxyoxaziridine salts (**40**). Significant quantities of the 5α-cholestane (**29**) in the photolysis of the 6α-nitro-5α-cholestane (**26**) may be formed directly from the latter,[3] which would be expected to have a low kinetic acidity, rather than its anion. In general, nitrocyclohexanes have lower kinetic acidities than nitrocyclopentanes[29] and the 6β-proton of the 6α-nitro-5α-cholestane would be relatively sterically hindered. It appears that hydroxamic acid formation occurs most efficiently when the nitro group is attached to a five-membered ring, but other factors must be involved in view of the relatively low yield of the 13α-hydroxamic acid (**13**). Release of intracyclic strain at the *trans* C/D-ring junction may be important in the 13β-compounds, as it appears to be in base-catalysed D-homoannelation of 17β-hydroxy-20-ketones.[30] The preferred migration of the more substituted C-13 carbon atom is a further common feature and these observations may be rationalised assuming the intermediacy of (**49**); this is analogous to (**50**) which is presumed to be involved in the base-catalysed D-homoannelations of 17-hydroxy-20-ketones. It is possible that

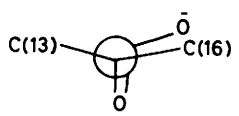


(**49**)

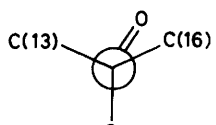


(**50**)

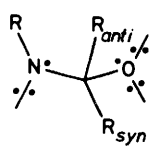
the conformer (**52**) of the intermediate (**49**) is involved in the rearrangement[4] since this would be easily arrived at from the anion of the *N*-hydroxyoxaziridine (**51**) which would be expected to have a preferred configuration in which the N–O$^-$ bond is *anti* to the C/D-ring junction. The photorearrangement of the *N*-butyl spiro-oxaziridine (**46**) appears to be stereoelectronically controlled in agreement with earlier[23,24] experimental and theoretical observations and some recent experimental work.[31] In all cases it appears that the group which is *anti* to the nitrogen lone pair in the oxaziridine migrates in an essentially concerted process in which the N–O bond-cleaved species (**53**) is short-lived.



(**51**)



(**52**)



(**53**)

Experimental

Solutions were dried ($MgSO_4$) and solvents were removed under reduced pressure on a rotary evaporator. Plates (1 m × 0.5 mm thick) of Kieselgel PF 254 (Merck) were used for preparative t.l.c. Degassed absolute ethanol was used for photolyses. I.r. spectra were determined with a Perkin-Elmer 177 spectrophotometer, ^1H n.m.r. spectra were determined in deuteriochloroform solution at 60 and 90 MHz with Varian EM360A and Perkin-Elmer R32 spectrometers, and mass spectra were recorded with AE1 MS12 and Kratos MS 50 and MS 80 spectrometers. M.p.s were recorded on a Kofler hot stage apparatus. Rotations were determined for chloroform solutions using an Optical Activity digital polarimeter. Ether refers to diethyl ether.

3β-*Acetoxy*-17ξ-*nitro*-5α,13α-*androstane* (**4**).—A solution of potassium hydrogen carbonate (0.65 g) in water (5 ml) was added to a vigorously stirred mixture of *N*-bromosuccinimide (1.2 g), dioxane (3 ml), and water (3 ml) followed by a solution of the oxime (**2**) (0.75 g; m.p. 164—166 °C) in dioxane (20 ml). The mixture was stirred at room temperature for 2 days during which time the initially formed blue colour changed to pale yellow. Water was added and the mixture was extracted with ether (×2). The combined ether extracts were washed successively with ferrous sulphate solution (10%) and water and dried. Removal of the solvent gave a residue which was taken up in tetrahydrofuran (15 ml) and water (5 ml). Sodium borohydride (0.25 g) was added during 15 min after which the solution was stirred for 1 h at room temperature. A further portion of sodium borohydride (0.1 g) was added, and after a further period of 1 h the solution was acidified with hydroxylamine hydrochloride and extracted with ether (×2). The combined ether extracts were washed with water and dried and removal of the solvent gave a pale yellow gum (0.7 g) which after preparative t.l.c., eluting with benzene–ethyl acetate (3:1), afforded the 17-*nitro compound* (**4**) (150 mg; 20%), m.p. 145—146 °C, $[\alpha]_D$ −33° (*c*, 5.0), $\nu_{max.}$($CHCl_3$) 1 735 (Me*CO*O), 1 540, and 1 370 cm^{-1} (NO_2); δ 0.80 (s, 13β-Me), 0.90 (s, 10β-Me), 2.0 (s, OAc), and 4.55 (m, 3- and 17-H) (Found: C, 69.1; H, 9.3; N, 3.7. $C_{21}H_{33}NO_4$ requires C, 69.4; H, 9.15; N, 3.85%).

20β-*Nitro*-5α-*pregnan*-3β-*ol* (**36**).—The 20β-amine (**35**)[18] (0.5 g) in chloroform (15 ml) was added dropwise to a boiling solution of MCPBA (2 g) in chloroform (15 ml). The reaction mixture was heated under reflux for 0.5 h and then allowed to cool, washed with saturated sodium sulphite solution, saturated sodium hydrogen carbonate solution, and water, and dried. Removal of the solvent followed by recrystallisation from methanol afforded the 20β-*nitropregnane* (**36**) (350 mg; 65%), m.p. 225—227 °C, $[\alpha]_D$ +11° (*c*, 10.0), $\nu_{max.}$($CHCl_3$) 3440 (OH), 1 550, and 1 380 cm^{-1} (NO_2); δ 0.75 (s, 13β-Me) 0.80 (s, 10β-Me), 3.5 (m, 3α-H), and 4.5 (m, 20α-H) (Found: $M^{+\cdot}$, 349.2599. $C_{21}H_{35}NO_3$ requires *M*, 349.2617).

Photolysis of the Nitro Compounds.—The nitro compound (100 mg), in a solution of absolute ethanol (100 ml) containing sodium ethoxide (10 equiv.), was photolysed using a low-pressure mercury lamp (3 W) in a water-cooled quartz apparatus. When the reaction was complete (assessed by t.l.c.) the solvent was removed and the residue was dissolved in a minimum volume of water. Acetic acid (1%) was added to bring th pH of the solution to *ca.* 6, after which the mixture was extracted with chloroform (×2) and the combined chloroform extracts were washed with water and dried. Removal of the solvent gave the crude product which was purified as indicated below.

17β-*Nitro compound* (**3**). The crude product, a yellow gum (100 mg) was crystallised from methanol to give the 3β,17a-*dihydroxy*-17a-*aza*-D-*homo*-5α-*androstan*-17-*one* (**12**) (60 mg) which was recrystallised to afford a pure sample (50 mg), m.p. 247—250 °C, $[\alpha]_D$ 0° (*c*, 5.0), $\nu_{max.}$(KBr) 3 350 (OH) and 1 620

cm^{-1} (*CO*NROH); δ 0.80 (s, 10β-Me), 1.27 (s, 13β-Me), and 3.61 (m, 3α-H) (Found: C, 70.8; H, 10.1; N, 4.35. $C_{19}H_{31}NO_3$ requires C, 71.0; H, 9.7; N, 4.35%). Preparative t.l.c. of the mother-liquors yielded the 17,18-cyclosteroid (**25**) (5 mg), m.p. 149—151 °C (lit.,[9] m.p. 149—151 °C) and a mixture (10 mg) ($\nu_{max.}$ 1 735 cm^{-1}) of the 13β-ketone (**8**) [δ 0.80 (br s, 10β- and 13β-Me)] and the 13α-ketone (**7**) [δ 0.63 (s, 10β-Me), 0.93 (s, 13α-Me)]. T.l.c. of authentic samples confirmed that the ketones (**7**) and (**8**) have very similar R_F values.

17β-*Nitro* Δ^5-*compound* (**10**). The crude product, a yellow gum (96 mg), was crystallised from methanol to give the 3β,17a-*dihydroxy*-17a-*aza*-D-*homoandrost*-5-*en*-17-*one* (**22**) (70 mg) which was recrystallised to afford a pure sample (60 mg), m.p. 227—229 °C, $[\alpha]_D$ −82° (*c*, 1.0); $\nu_{max.}$($CHCl_3$) 3 400 (OH) and 1 610 cm^{-1} (*CO*NROH); δ 1.0 (s, 10β-Me), 1.25 (s, 13β-Me), 3.55 (m, 3α-H), and 5.3 (m, 6-H) (Found: $M^{+\cdot}$, 319.2146. $C_{19}H_{20}NO_3$ requires *M*, 319.2147).

17ξ-*Nitro* 13α-*compound* (**4**). The crude product, a yellow gum (100 mg), was separated into two fractions by preparative t.l.c. eluting with benzene–ethyl acetate (3:1). The more polar fraction (30 mg) was crystallised from methanol to afford the 3β,17a-*dihydroxy*-17a-*aza*-D-*homo*-5α,13α-*androstan*-17-*one* (**13**), m.p. 130—131 °C, $\nu_{max.}$($CHCl_3$) 3 350 (OH) and 1 610 cm^{-1} (*CO*NROH); δ 0.72 (s, 10β-Me), 1.37 (s, 13β-Me), and 3.53 (m, 3α-H) (Found: $M^{+\cdot}$, 321.2302. $C_{19}H_{31}NO_3$ requires *M*, 321.2304). The less polar fraction (50 mg) was identified as a mixture of the 13β-ketone (**8**) [δ 0.80 (br s, 10β- and 13β-Me)] and the 13α-ketone (**7**) [major component δ 0.63 (s, 10β-Me) and 0.93 (s, 13α-Me)].

6α-*Nitro compound* (**26**). The crude product, a yellow gum (100 mg) was separated into four fractions by preparative t.l.c. eluting with benzene–ethyl acetate (2:1). The alkene-containing fraction (30 mg) was further subjected to preparative t.l.c. (benzene–ethyl acetate, 2:1) on silver nitrate (10%) impregnated silica to afford cholesterol (**27**) (15 mg), m.p. and mixed m.p. 146—148 °C, and a minor component (3 mg) which was not identified. The second fraction (25 mg) was crystallised from methanol to afford 3β-hydroxy-5α-cholestan-6-one (**28**) (20 mg), m.p. 142—144 °C (lit.,[13] m.p. 143 °C); $\nu_{max.}$($CHCl_3$) 1 705 cm^{-1} (C=O); 3-*O*-acetyl derivative, m.p. 126—128 °C (lit.,[13] m.p. 128 °C). The third fraction (20 mg) was crystallised from methanol to afford 3β-hydroxy-5α-cholestane (**29**), m.p. and mixed m.p. 138—140 °C (lit.,[14] m.p. 142 °C). The fourth fraction (15 mg) was crystallised from methanol to give a solid (5 mg), tentatively identified as the hydroxamic acid (**30**), m.p. 220 °C (decomp.), $\nu_{max.}$($CHCl_3$) 3 300—3 400 (OH) and 1 660 cm^{-1} (*CO*NHOH) (Found: $[M - 16]^{+\cdot}$ 417. $C_{27}H_{47}NO_3$ requires $[M - 16]$ 417).

3β-*Nitro compound* (**32**). The crude product, a yellow gum (100 mg), separated into three fractions by preparative t.l.c. eluting with toluene–ethyl acetate (2:1). The least polar fraction (130 mg) was crystallised from methanol to afford 5α-cholest-2-ene (**33**) (20 mg), m.p. 68—70 °C (lit.,[17] m.p. 75 °C, no depression of mixed m.p.). A second fraction (15 mg) was identified as 5α-cholestan-3-one (**34**), $\nu_{max.}$($CHCl_3$) 1 710 cm^{-1} (C=O); δ 0.70 (s, 13β-Me), 0.83 (s, 10β-Me), by comparison with authentic material although it was not crystallised. The remainder was largly polymeric material.

20β-*Nitro compound* (**36**). The crude product, a yellow gum (95 mg), was separated into two fractions by preparative t.l.c. eluting with toluene–ethyl acetate 2:1. The less polar alkene fraction (30 mg) was further purified by preparative t.l.c. on silver nitrate (10%) impregnated silica (toluene–ethyl acetate, 2:1) to afford the major component (18 mg) which crystallised from aqueous methanol to afford (*E*)-3β-hydroxy-5α-pregn-17(20)-ene (15 mg) (**38**), m.p. 132—134 °C (lit.,[20] 136—137 °C), 3-*O*-acetyl derivative m.p. 117—119 °C (lit.,[21] m.p. 120—121 °C). The more polar fraction (20 mg) was identified as 3β-hydroxy-5α-pregnan-20-one (**37**), $\nu_{max.}$($CHCl_3$) 3 400 (OH) and 1 720 cm^{-1} (C=O); δ 0.55 (s, 13β-Me), 0.8 (s, 10β-Me), and 2.1 (s, 20-Me), by comparison with authentic material, although it was not crystallised.

Conversion of the Hydroxamic Acid (**12**) *into the Lactam* (**14**).—A solution of the hydroxamic acid (**12**) (50 mg) in acetic acid (20 ml) was heated under reflux with zinc powder (250 mg) for 6 h after which the reaction mixture was filtered and the solids were washed with a small volume (×3) of acetic acid. The combined filtrate and washings were poured onto ice and the resultant mixture was extracted with methylene dichloride (×3). The combined organic extracts were washed with saturated sodium hydrogen carbonate solution until neutral and then with water and dried. The solvent was removed to afford an oily residue which was taken up in pyridine (1.5 ml) and acetic anhydride (0.2 ml). The solution was allowed to stand at room temperature overnight and poured onto ice, after which the resultant solid was removed by filtration and washed thoroughly with water. The dry solid was crystallised from acetone–light petroleum (b.p. 40—60 °C) to afford 3β-acetoxy-17a-aza-D-homo-5α-androstan-17-one (**14**) (40 mg; 74%), m.p. 277—280 °C (lit.,[10] m.p. 275—277 °C).

In a further experiment, the crude photolysate from the 17β-nitro compound (**3**) (100 mg) was reduced and acetylated as above to afford a crude product (100 mg) which was crystallised from methanol to afford the lactam (**14**) (60 mg), m.p. 277—280 °C. Examination of the mother liquor by t.l.c. and ^1H n.m.r. spectrometry did not provide evidence of any other lactam.

3β-*Hydroxy*-17a-*methoxy*-17a-*aza*-D-*homo*-5α-*androstan*-17-*one* (**15**).—A mixture of the hydroxamic acid (**12**) (25 mg), NaH (5 mg), and DMF (20 ml) was stirred under nitrogen at room temperature for 1 h. Methyl iodide (0.1 g) was added and the mixture was stirred under nitrogen at room temperature overnight, then water was added and the product was extracted into ether (×2). The combined ether extracts were washed with water and dried; removal of the solvent and crystallisation of the residue (20 mg) from acetone–light petroleum (b.p. 40—60 °C) gave the O-*methyl derivative* (**15**) (15 mg; 58%), m.p. 235—236 °C, $\nu_{max.}$($CDCl_3$) 3 420 (OH) and 1 665 cm^{-1} (*CO*NROMe); δ 0.80 (s, 10β-Me), 1.20 (s, 13β-Me), 3.5 (m, 3α-H), and 3.72 (s, NOMe) (Found: $M^{+\cdot}$, 335.2451. $C_{20}H_{33}NO_3$ requires *M*, 33.2460).

3β,17a-*Diacetoxy*-17a-*aza*-D-*homo*-5α-*androstan*-17-*one* (**16**).—Acetylation of the hydroxamic acid (**12**) (25 mg) with acetic anhydride (1 ml) and pyridine (10 ml) at room temperature overnight followed by the normal work-up provided a crude product which crystallised from methanol to give the *di*-O-*acetyl derivative* (**16**) (25 mg; 80%), m.p. 215—217 °C, $[\alpha]_D$ +23° (*c*, 10.0); $\nu_{max.}$($CHCl_3$) 1 800 (CONRO*CO*Me), 1 735 (Me*CO*O), and 1 670 cm^{-1} (*CO*NROCOMe); δ 0.80 (s, 10β-Me), 1.22 (s, 13β-Me), 2.00 (s, 3-OAc), 2.16 (s, NROAc), and 4.7 (m, 3α-H) (Found: C, 68.0; H, 9.0; N, 3.5%; $M^{+\cdot}$, 405.2504. $C_{23}H_{35}NO_5$ requires C, 68.1; H, 8.6; N, 3.5%; *M*, 405.2515).

3β,17a-*Diacetoxy*-17a-*aza*-D-*homoandrost*-5-*en*-17-*one* (**23**).—Acetylation of the hydroxamic acid (**22**) (50 mg) as above afforded the *di*-O-*acetyl derivative* (**23**) (55 mg; 87%), m.p. 196—197 °C (from methanol); $\nu_{max.}$($CHCl_3$) 1 790 (CONRO*CO*Me), 1 735 (Me*CO*O), and 1 670 cm^{-1} (*CO*NROCOMe); δ 1.0 (s, 10β-Me), 1.25 (s, 13β-Me), 2.02 (s, 3-OAc), 2.15 (s, NROAc), 4.5 (m, 3α-H), and 5.3 (m, 6-H) (Found: C, 68.8; H, 8.4; N, 3.4. $C_{23}H_{33}NO_5$ requires C, 68.4; H, 8.2; N, 3.5%).

Conversion of the Hydroxamic Acid (**22**) *into the Lactam* (**24**).—Reduction and acetylation of the crude photolysate from

the 17β-nitro Δ^5-compound (**10**) (100 mg), as for that from the 17β-nitro compound (**3**), and crystallisation of the resultant residue (100 mg) from methanol afforded 3β-acetoxy-17a-aza-D-homoandrost-5-en-17-one (**24**) (65 mg; 68%), m.p. 298—300 °C (lit.,[10] m.p. 295—298 °C). No evidence of any other lactam component could be detected in the product by t.l.c. and ^{1}H n.m.r. spectrometry.

3β,17a-*Diacetoxy*-17a-*aza*-D-*homo*-5α,13α-*androstan*-17-*one* (**17**).—The crude photolysate (100 mg) from the 17ξ-nitro 13α-compound (**4**) (100 mg) was acetylated as above, and preparative t.l.c., eluting with benzene–ethyl acetate 3:1, gave three fractions. The most polar fraction (40 mg) was crystallised from methanol to afford the di-*O*-acetyl derivative (**17**) (30 mg; 27%), m.p. 195—196 °C, $[\alpha]_D$ −47° (*c*, 5.0); $\nu_{max.}$($CHCl_3$) 1 790 (CONROC*O*Me), 1 735 (Me*CO*O), and 1 670 cm^{-1} (*CO*NROCOMe); δ 0.80 (s, 10β-Me), 1.3 (s, 13β-Me), 2.0 (s, 3-OAc), 2.15 (s, NROAc), and 4.65 (m, 3α-H) (Found: C, 67.8; H, 8.7; N, 3.2%; $M^{+\cdot}$, 405.2513. $C_{23}H_{35}NO_5$ requires C, 68.1; H, 8.7; N, 3.5%; *M*, 405.2515). The least polar fraction was 3β-acetoxy-5α,13α-androstan-17-one (**5**) (20 mg), m.p. 129—131 °C (lit.,[7] m.p. 133 °C, no depression of mixed m.p.). An intermediate fraction (25 mg) was a mixture of the 13β-ketone (**6**) [δ 0.82 (br s, 10β- and 13β-Me)] and the 13α-ketone (**5**) [δ 0.64 (s, 10β-Me) and 0.93 (s, 13β-Me)]. T.l.c. on authentic materials confirmed that the ketones (**5**) and (**6**) have similar R_F values.

3β-*Acetoxy*-2′-*butyl*-5α-*androstane*-17-*spiro*-3′-*oxa*-*ziridine* (**46**).—A solution of the 17-ketone (**6**) (250 mg) in benzene (50 ml) containing PTSA (20 mg) and butylamine (2 ml) was heated under reflux overnight using a Dean and Stark trap. The solution was allowed to cool, washed with saturated sodium hydrogen carbonate solution and water, dried and evaporated to give the crude *N*-butylimine (**45**) as a pale yellow gum (280 mg; 90%), $\nu_{max.}$($CHCl_3$) 1 730 (Me*CO*O) and 1 675 cm^{-1} (>C=N–); δ 0.80 (s, 10β-Me), 0.86 (s, 13β-Me), 1.95 (s, 3-OAc), 3.2 (t, *J* 7 Hz, =N–*CH*$_2$CH$_2$R), and 4.5 (m, 3α-H) (Found: $M^{+\cdot}$, 387. $C_{25}H_{41}NO_2$ requires *M*, 387). The freshly prepared *N*-butylimine (200 mg) in benzene (25 ml) was cooled to 5 °C and ethanol (3 ml) was added followed by a solution of MCPBA (110 mg) in benzene (5 ml). The reaction mixture was stirred in the dark at room temperature for 2 h, after which it was washed with saturated sodium sulphite solution, saturated sodium hydrogen carbonate solution, and water and dried. Removal of the solvent gave a pale yellow gum (200 mg) which was subjected to preparative t.l.c., eluting with toluene–ethyl acetate 3:1, and afforded the N-*butyl spiro-oxaziridine* (**46**) (145 mg; 70%), $\nu_{max.}$($CHCl_3$) 1 735 cm^{-1} (Me*CO*O); δ 0.82 (br s, 10β- and 13β-Me), 2.02 (s, 3-OAc), 2.7 (t, *J* 7 Hz >C(O)–N*CH*$_2$CH$_2$R), and 4.7 (m, 3α-H) (Found: $M^{+\cdot}$, 403.3101. $C_{25}H_{41}NO_3$ requires *M*, 403.3086), and the 17-ketone (**6**) (25 mg; 15%), m.p. 94—96 °C (lit.,[7] m.p. 95—97 °C).

Photolysis of the N-*Butyl Spiro-oxaziridine* (**46**).—The *N*-butyl spiro-oxaziridine (120 mg) in ethanol (100 ml) was photolysed under the usual conditions, for 3 h. Removal of the solvent and preparative t.l.c. of the residue (115 mg) eluting with toluene–ethyl acetate (5:1) afforded 3β-*acetoxy*-17-*butyl*-17-*aza*-D-*homo*-5α-*androstan*-17a-*one* (**47**) (70 mg) which on crystallisation from methanol, gave a pure sample (60 mg), m.p. 121—122 °C, $\nu_{max.}$($CHCl_3$) 1 735 (Me*CO*O) and 1 620 cm^{-1} (R_2NCO); δ 0.80 (s, 10β-Me), 1.06 (s, 13β-Me), 2.0 (s, 3-OAc), 3.25 (m, 16- and N-CH_2) and 4.65 (m, 3α-H) (Found: C, 74.4; H, 10.6; N, 3.5%; $M^{+\cdot}$, 403.3092. $C_{25}H_{41}NO_3$ requires C, 74.4; H, 10.2; N, 3.5%; *M*, 403.3087). A second minor fraction was the 17-ketone (**6**) (25 mg), m.p. 96—98 °C (lit.,[7] m.p. 95—97 °C).

3β-*Acetoxy*-17a-*butyl*-17-*aza*-D-*homo*-5α-*androstan*-17-*one* (**21**).—The lactam (**18**) (300 mg) was converted under standard conditions[32] into its tetrahydropyranyl ether (**19**) which, without purification, was dissolved in DMF (20 ml) to which sodium hydride (90 mg) was added. The mixture was stirred under nitrogen at room temperature for 1 h, and freshly distilled butyl iodide (1 ml) then added. After a further 24 h, methanol was added to destroy the excess of sodium hydride and the mixture was diluted with water and extracted with ether (×2). The combined ether extracts were washed with water, dried and evaporated to give the crude *N*-butyl lactam (**20**) (200 mg). Successive treatment of this with methanol–PTSA under reflux, and acetic anhydride–pyridine at room temperature, afforded, after work-up and preparative t.l.c. eluting with toluene–ethyl acetate 3:1, the N-*butyl lactam* (**21**) as a gum (105 mg; 30%), $\nu_{max.}$($CHCl_3$) 1 735 (Me*CO*O) and 1 620 cm^{-1} (R_2NCO); δ 0.80 (s, 10β-Me), 1.12 (s, 13β-Me), 2.02 (s, 3-OAc), 2.4 (m, 16-CH_2), 2.9 and 3.5 (2 × 1 H, m, NCH_2), and 4.65 (m, 3α-H) (Found: $M^{+\cdot}$, 403.3083. $C_{25}H_{41}NO_3$ requires *M*, 403.3087).

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