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Photochemical Reactions. 21.[1] Sensitized Photooxygenation of *N*-Methylated 4-Aza-5-androsten-3-one and 4-Aza-5-androstene Steroidal Systems[2]

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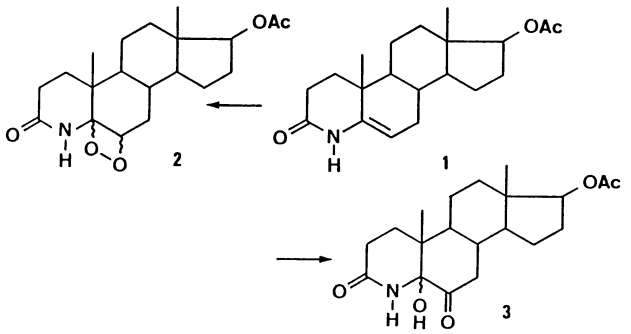
Two steroidal ene lactams, *N*-methyl-4-aza-5-androsten-3,17-dione and *N*-methyl-6-methoxy-4-aza-5-androsten-3,17-dione, and an enamine, *N*-methyl-4-aza-5-androsten-17β-ol, have been synthetized and their sensitized photooxygenations were investigated. The two ene lactams yield fragmentation compounds via the corresponding dioxetanes. Comparison with the previously reported behavior of an analogous *N*-unsubstituted ene lactam, seems to indicate that *N*-substitution is essential for the fragmentation to take place. On the other hand, the enamine yields a ketol. All results are briefly discussed from the mechanistic point of view.

Some years ago we published that the photooxygenation of 17β-acetoxy-4-aza-5-androsten-3-one (**1**) yields, among other products, 17β-acetoxy-5ξ,6ξ-epidioxy-4-azaandrostan-3-one (**2**) and 17β-acetoxy-5ξ-hydroxy-4-azaandrostan-3,6-dione (**3**) (Scheme 1).[3] The dioxetane readily isomerizes to **3**, and was therefore thought to be an intermediate in the transformation **1**→**3**. On the other hand, neither chemiluminescence nor the typical fragmentation to a dicarbonyl compound, were observed when heating **2**. This somewhat anomalous behavior for a 1,2-dioxetane,[4] suggested the necessity of investigating those structural details of the molecule which could be responsible for it. With the purpose of studying their photooxygenation, we decided to synthesize compounds **6**, **9**, and **11** (Scheme 2), which show the following structural modifications:



Scheme 1.

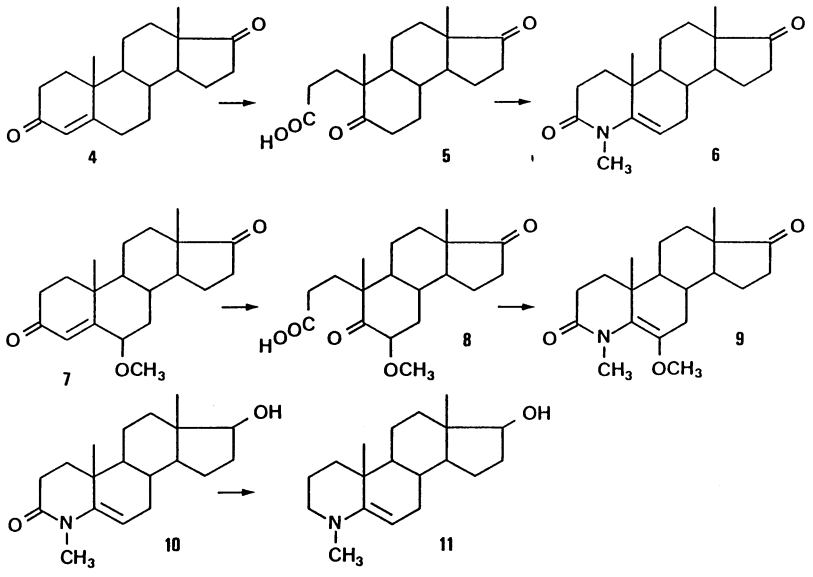
(a) *N*-Substitution

(b) Higher electronic density of the double bond (cf. **9**), and

(c) Suppresion of the carbonyl group at C-3, to an enamine (cf. **11**)

Results

Synthesis of the Heterocyclic Steroids. Starting materials for the synthesis of lactams **6** and **9** were, respectively, 4-androsten-3,17-dione (**4**)[5] and 6β-methoxy-4-androsten-3,17-dione (7).[6] Successive von



Scheme 2.

Table 1. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Factors ($Å^2$) for **9** (Standard Deviations in Parentheses)

Atom	X/A	Y/B	Z/C	B_{eq}	Atom	X/A	Y/B	Z/C	B_{eq}
C(1)	6570(5)	1421(4)	3608(4)	5.59	C(13)	9530(4)	4889(4)	3449(3)	4.63
C(2)	5460(5)	774(4)	3374(5)	6.14	C(14)	8510(4)	5148(4)	4127(3)	4.30
C(3)	4331(5)	1366(4)	3451(3)	5.13	C(15)	8538(4)	6422(4)	4269(4)	5.51
N(4)	4340(3)	2529(3)	3610(3)	4.81	C(16)	9867(5)	6664(5)	4349(5)	6.21
C(5)	5392(4)	3149(3)	3802(3)	3.88	C(17)	10453(4)	5667(6)	3876(4)	6.09
C(6)	5392(3)	4019(3)	4394(3)	4.13	C(18)	9353(4)	5332(5)	2379(3)	6.10
C(7)	6427(4)	4797(4)	4555(3)	4.70	C(19)	6355(5)	2811(4)	2177(3)	4.92
C(8)	7377(3)	4576(3)	3801(3)	3.74	O(20)	3425(4)	870(3)	3320(3)	7.00
C(9)	7576(4)	3297(3)	3713(3)	4.27	C(21)	3254(5)	3131(5)	3458(4)	6.14
C(10)	6502(4)	2692(3)	3313(3)	4.03	O(22)	4412(3)	4218(3)	4990(2)	5.02
C(11)	8683(4)	2991(5)	3128(5)	6.25	C(23)	3980(4)	5356(4)	5021(4)	5.58
C(12)	9777(4)	3653(5)	3474(5)	6.25	O(24)	11503(3)	5519(4)	3844(5)	8.85

Table 2. Bond Distances (l/Å) for **9** (Standard Deviations in Parentheses)

C(2)-C(1)	1.52(1)	C(10)-C(9)	1.52(1)
C(10)-C(1)	1.56(1)	C(11)-C(9)	1.54(1)
C(3)-C(2)	1.48(1)	C(19)-C(10)	1.56(1)
N(4)-C(3)	1.40(1)	C(12)-C(11)	1.55(1)
O(20)-C(3)	1.21(1)	C(13)-C(12)	1.49(1)
C(5)-N(4)	1.44(1)	C(14)-C(13)	1.52(1)
C(21)-N(4)	1.45(1)	C(17)-C(13)	1.52(1)
C(6)-C(5)	1.31(1)	C(18)-C(13)	1.56(1)
C(10)-C(5)	1.53(1)	C(15)-C(14)	1.52(1)
C(7)-C(6)	1.52(1)	C(16)-C(15)	1.55(1)
O(22)-C(6)	1.40(1)	C(17)-C(16)	1.50(1)
C(8)-C(7)	1.52(1)	O(24)-C(17)	1.22(1)
C(9)-C(8)	1.54(1)	C(23)-O(22)	1.44(1)
C(14)-C(8)	1.53(1)		

Table 3. Bond Angles (θ/°) for **9** (Standard Deviations in Parentheses)

C(10)-C(1)-C(2)	113(1)	C(9)-C(10)-C(1)	109(1)
C(3)-C(2)-C(1)	119(1)	C(9)-C(10)-C(5)	110(1)
N(4)-C(3)-C(2)	118(1)	C(19)-C(10)-C(1)	110(1)
O(20)-C(3)-C(2)	121(1)	C(19)-C(10)-C(5)	108(1)
O(20)-C(3)-N(4)	121(1)	C(19)-C(10)-C(9)	113(1)
C(5)-N(4)-C(3)	123(1)	C(12)-C(11)-C(9)	113(1)
C(21)-N(4)-C(3)	117(1)	C(13)-C(12)-C(11)	110(1)
C(21)-N(4)-C(5)	120(1)	C(14)-C(13)-C(12)	109(1)
C(6)-C(5)-N(4)	121(1)	C(17)-C(13)-C(12)	117(1)
C(10)-C(5)-N(4)	116(1)	C(17)-C(13)-C(14)	101(1)
C(10)-C(5)-C(6)	123(1)	C(18)-C(13)-C(12)	112(1)
C(7)-C(6)-C(5)	125(1)	C(18)-C(13)-C(14)	113(1)
O(22)-C(6)-C(5)	119(1)	C(18)-C(13)-C(17)	104(1)
O(22)-C(6)-C(7)	116(1)	C(13)-C(14)-C(8)	113(1)
C(8)-C(7)-C(6)	111(1)	C(15)-C(14)-C(8)	120(1)
C(9)-C(8)-C(7)	109(1)	C(15)-C(14)-C(13)	105(1)
C(14)-C(8)-C(7)	110(1)	C(16)-C(15)-C(14)	102(1)
C(14)-C(8)-C(9)	109(1)	C(17)-C(16)-C(15)	105(1)
C(10)-C(9)-C(8)	112(1)	C(16)-C(17)-C(13)	109(1)
C(11)-C(9)-C(8)	113(1)	O(24)-C(17)-C(13)	126(1)
C(11)-C(9)-C(10)	112(1)	O(24)-C(17)-C(16)	125(1)
C(5)-C(10)-C(1)	106(1)	C(23)-O(22)-C(6)	117(1)

Rudloff fragmentation[7] to the seco-carboxylic acids **5** and **8**, and condensation with methylamine, yielded the lactams in 40—70% yield (Scheme 2). An X-ray analysis confirmed the structure of **9**. Lithium aluminium hydride reduction of lactam **10**,[8] gave the enamine **11** in 88% yield.

Crystal Data of 9, Structure Solution and Refinement. Suitable crystals of **9** ($C_{20}H_{29}O_3N$) were obtained by slow evaporation of an acetone-petroleum ether solution. The single crystal was mounted on a four-circle diffractometer (Syntex $P2_1$). Unit cell dimensions were as follows: a=11.466(5); b=11.848 (5); c=13.567(6) Å. Space group $P2_12_12_1$ (Z=4). Intensities were collected with Cu K_α radiation (λ=1.54178 Å) monochromatized by a graphite single crystal, using ω-scan technique.

Of 1443 reflections measured, 1382 were considered significant $I \geqslant 2.5\sigma(I)$. After the Lorentz-polarization corrections were applied, the structure was determined by direct methods (MULTAN program[9]). The atomic parameters were refined using SHELX program[10] (full matrix least-squares). The positions of H-atoms were calculated and floated on the adjacent C-atoms assuming C-H=1.08 Å. The final conventional R value was 0.061. Atomic coordinates and equivalent isotropic temperature factors are listed in Table 1, bond distances and angles in Tables 2 and 3 respectively.** Figure 1[11] is a drawing of the molecule with the numbering scheme.

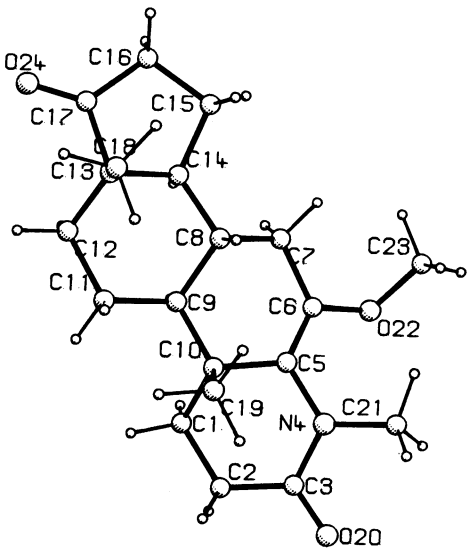
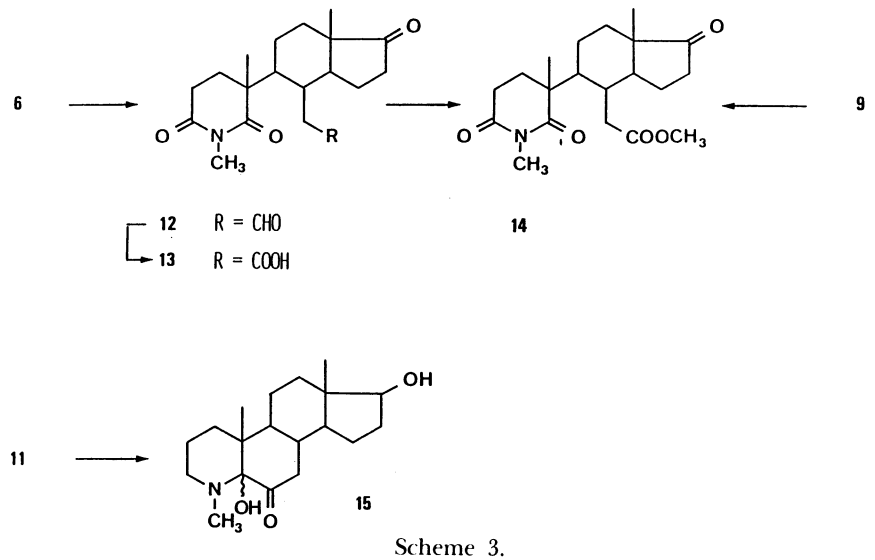


Fig. 1. Perspective view of molecule **9** with numbering scheme.



Scheme 3.

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Factors (Å^2) for **14** (Standard Deviations in Parentheses)

Atom	X/A	Y/B	Z/C	B_{eq}	Atom	X/A	Y/B	Z/C	B_{eq}
C(1)	4623(8)	5798(6)	9190(1)	4.08	C(14)	5461(7)	2264(5)	8326(1)	3.42
C(2)	4501(10)	6780(6)	9541(1)	5.06	C(15)	4369(11)	2073(6)	7942(1)	4.80
C(3)	5167(11)	5913(7)	9882(2)	5.38	C(16)	4301(12)	323(6)	7908(2)	5.77
N(4)	6883(8)	4920(5)	9830(1)	4.76	C(17)	4343(9)	−263(5)	8306(2)	4.49
C(5)	8028(9)	4748(6)	9495(1)	4.05	C(18)	2065(8)	1312(6)	8684(2)	4.55
C(6)	8230(9)	5140(6)	8080(1)	3.95	C(19)	8432(8)	6400(6)	8958(1)	4.38
C(7)	5949(8)	5065(5)	8238(1)	3.54	O(20)	4336(9)	6112(7)	10188(1)	8.37
C(8)	5423(7)	3811(4)	8517(1)	3.08	C(21)	7805(14)	4139(8)	10161(2)	7.38
C(9)	6832(8)	3710(5)	8878(1)	3.21	O(22)	8513(6)	6434(4)	7900(1)	5.74
C(10)	6893(7)	5177(5)	9126(1)	3.42	C(23)	10602(11)	6675(9)	7734(2)	7.09
C(11)	6076(9)	2352(5)	9126(1)	3.96	O(24)	4235(10)	−1561(4)	8391(1)	7.03
C(12)	5874(8)	869(5)	8921(1)	3.88	O(25)	9819(6)	4196(5)	9500(1)	5.31
C(13)	4463(8)	1044(5)	8574(1)	3.56	O(26)	9584(7)	4179(5)	8093(1)	6.67

Photooxygenation of 6, 9, and 11. The three photooxygenations were carried out in dry benzene solution, with Rose Bengal adsorbed on silica gel as sensitizer[12] (alternatively, polymer-immobilized Rose Bengal, Sensitox,[13] can be used), and a Sylvania 500 watts tungsten-iodine lamp. Lactam **6** yielded one main compound which was identified as the seco-keto aldehyde **12** (46%) (Scheme 3). Jones oxidation of **12** followed by CH_2N_2 treatment, gave the seco-keto ester **14** (**12**→**13**→**14**). This compound was also directly obtained, in 40% yield, by the photosensitized oxygenation of **9**. In this case, a second more polar product was detected by TLC, which with the time evolved towards **14**. The structure of **14** was confirmed by an X-ray analysis.

Crystal Data of 14, Structure Solution and Refinement. A single crystal of **14** was mounted on a Syntex $P2_1$ diffractometer. Cell parameters: a=6.128(2); b=8.929(5); c=35.551(14) Å. Space group $P2_12_12_1$ (Z=4). Intensity data were measured using the same technique as for compound **9**. Of 1576 reflections measured, 1416 ($I \geqslant 2.5\sigma(I)$) were considered reliable and used in the crystal structure analysis. After the Lorentz-polarization corrections were applied the structure was determined by direct methods, (MULTAN program[9]). The atomic parameters were refined by full matrix least-squares calculations (SHELX program[10]). The positions of H-atoms were calculated and floated on the adjacent C-atoms assuming C-H=1.08Å. The final conventional R value was 0.051. Atomic coordinates and equivalent isotropic temperature factors are listed in Table 4, bond distances and angles in Tables 5 and 6 respectively.** Figure 2[11] is a drawing of the molecule with the numbering scheme.

Photooxygenation of **11** yielded the keto alcohol **15** in 22% yield. The structure of **15** is tentatively assigned on the basis of its spectral data: The chemical shift of the 19-methyl group in the ^{1}H NMR spectrum appears at a very high field (δ 0.70) in agreement with the presence of a carbonyl at C(6);[14] on the other hand the IR spectrum exhibits a carbonylic band at 1710 cm^{-1}.

The isolation of the fragmentation compounds **12** and **14** from **6** and **9**, points towards the intermediacy

**The anisotropic thermal parameters of non-hydrogen atoms, the parameters of hydrogen atoms, and the tables of the observed and the calculated structure factors were kept at the Chemical Society of Japan (as Doc. No. 8712).

Table 5. Bond Distances (l/Å) for **14** (Standard Deviations in Parentheses)

C(2)-C(1)	1.52(1)	C(14)-C(8)	1.54(1)
C(10)-C(1)	1.51(1)	C(10)-C(9)	1.58(1)
C(3)-C(2)	1.50(1)	C(11)-C(9)	1.57(1)
N(4)-C(3)	1.39(1)	C(19)-C(10)	1.56(1)
O(20)-C(3)	1.21(1)	C(12)-C(11)	1.52(1)
C(5)-N(4)	1.39(1)	C(13)-C(12)	1.52(1)
C(21)-N(4)	1.48(1)	C(14)-C(13)	1.53(1)
C(10)-C(5)	1.53(1)	C(17)-C(13)	1.51(1)
O(25)-C(5)	1.20(1)	C(18)-C(13)	1.54(1)
C(7)-C(6)	1.51(1)	C(15)-C(14)	1.53(1)
O(22)-C(6)	1.33(1)	C(16)-C(15)	1.57(1)
O(26)-C(6)	1.19(1)	C(17)-C(16)	1.51(1)
C(8)-C(7)	1.53(1)	O(24)-C(17)	1.20(1)
C(9)-C(8)	1.55(1)	C(23)-O(22)	1.43(1)

Table 6. Bond Angles (θ/°) for **14** (Standard Deviations in Parentheses)

C(10)-C(1)-C(2)	112(1)	C(9)-C(10)-C(1)	111(1)
C(3)-C(2)-C(1)	111(1)	C(9)-C(10)-C(5)	106(1)
N(4)-C(3)-C(2)	115(1)	C(19)-C(10)-C(1)	111(1)
O(20)-C(3)-C(2)	123(1)	C(19)-C(10)-C(5)	103(1)
O(20)-C(3)-N(4)	122(1)	C(19)-C(10)-C(9)	112(1)
C(5)-N(4)-C(3)	125(1)	C(12)-C(11)-C(9)	115(1)
C(21)-N(4)-C(3)	119(1)	C(13)-C(12)-C(11)	110(1)
C(21)-N(4)-C(5)	116(1)	C(14)-C(13)-C(12)	108(1)
C(10)-C(5)-N(4)	118(1)	C(17)-C(13)-C(12)	117(1)
O(25)-C(5)-N(4)	120(1)	C(17)-C(13)-C(14)	102(1)
O(25)-C(5)-C(10)	122(1)	C(18)-C(13)-C(12)	111(1)
O(22)-C(6)-C(7)	110(1)	C(18)-C(13)-C(14)	115(1)
O(26)-C(6)-C(7)	127(1)	C(18)-C(13)-C(17)	104(1)
O(26)-C(6)-O(22)	123(1)	C(13)-C(14)-C(8)	112(1)
C(8)-C(7)-C(6)	118(1)	C(15)-C(14)-C(8)	119(1)
C(9)-C(8)-C(7)	117(1)	C(15)-C(14)-C(13)	105(1)
C(14)-C(8)-C(7)	112(1)	C(16)-C(15)-C(14)	101(1)
C(14)-C(8)-C(9)	108(1)	C(17)-C(16)-C(15)	106(1)
C(10)-C(9)-C(8)	115(1)	C(16)-C(17)-C(13)	109(1)
C(11)-C(9)-C(8)	110(1)	O(24)-C(17)-C(13)	126(1)
C(11)-C(9)-C(10)	109(1)	O(24)-C(17)-C(16)	125(1)
C(5)-C(10)-C(1)	112(1)	C(23)-O(22)-C(6)	116(1)

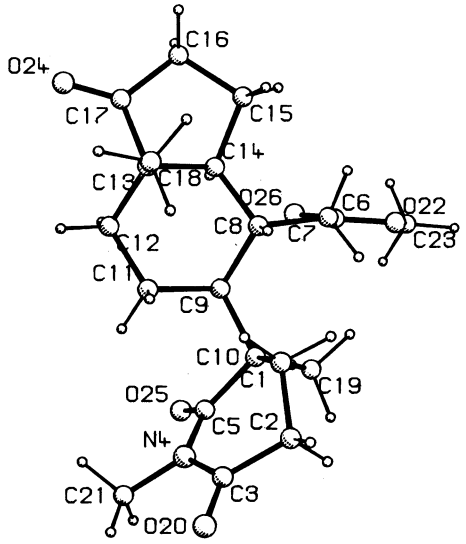
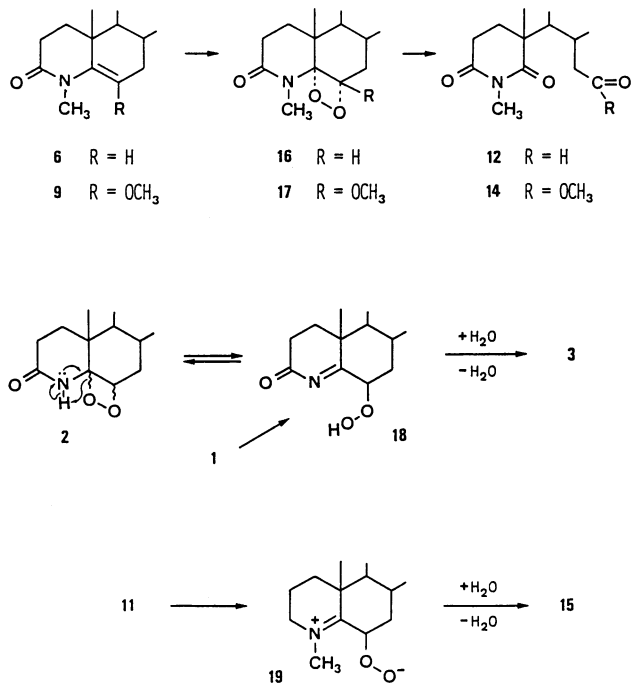


Fig. 2. Perspective view of molecule **14** with numbering scheme.

of the 1,2-dioxetanes **16** and **17**, respectively (Scheme 4). In fact, **16** and **17** have been obtained in quantitative yield in low temperature experiments,[15] and characterized by ^{1}H (300 MHz) and ^{13}C NMR and also by their conversion to the cleavage products **12** and **14** upon heating.[16]



Scheme 4.

Concerning the objectives of our work, the results obtained suggest that in the case of the lactams, the evolution of the dioxetanes towards fragmentation compounds or alternatively towards a ketol derivative, depends on the absence or presence of a hydrogen attached to the nitrogen atom. The anomalous behavior of the dioxetane **2** could be explained assuming a preferential isomerization to the ketol **3**, as shown in Scheme 4 (**2**⇄**18**→**3**), which in the absence of the N-H would not take place (no ketol was detected in the crude photooxygenation mixtures of **6** or **9**). Compound **3** could be also directly formed from **1** via the allylic hydroperoxide **18**.

In the case of the enamine **11**, no fragmentation products have been detected and this result is different from those described in the literature: Usually enamines yield fragmentation compounds via dioxetanes.[17] In the case of **11**, a zwitterionic intermediate of type **19** is proposed,[18] although its formation via dioxetane is not excluded. The difference in behavior between the lactams **6** and **9** and the enamine **11** can be explained by means of the availability of the lone pair electron of amine.

Experimental

General Remarks. By extraction in the usual way is meant: Dilution of the reaction mixture with ethyl acetate, washing of the organic phase with concentrated NaCl solution till neutral, drying on anhydrous Na_2SO_4 and evaporation under reduced pressure with a rotatory evaporator.

Silica gel Merck 0.063—0.2 mm, was used for column

chromatography (ratio to substance, 100:1). Thin-layer chromatography was performed using Merck Silica Gel 60F-254 plates. Spots were detected by direct observation under UV light (253.7 nm) or with 50% sulfuric acid spray followed by heating at 150 °C during 1 min.

Crystallizations were carried out in acetone-petroleum ether (bp 50—70 °C). Melting points were determined in an open capillary (Büchi-Tottoli apparatus) and are uncorrected.

Infrared spectra (KBr) were recorded on a Perkin-Elmer 683 spectrophotometer; absorption is given in ν values (cm^{-1}). The ultraviolet spectra (in Merck Ethanol UVASOL solution) were recorded on a Perkin-Elmer 124 spectrophotometer; absorption is given in λ_{max} (nm) values, followed by the ε value in brackets. Perkin-Elmer R-24 or Varian XL-100 spectrometers were used to obtain the ^{1}H NMR spectra (in $CDCl_3$ solution, unless otherwise specified). Chemical shifts (δ values) are reported relative to TMS as an internal standard. Coupling constants (J) are given in Hz. Multiplicities are expressed as: singlet (s), doublet (d), triplet (t), quartet (qa), multiplet (m), and broad signal (br). Mass spectra were measured on a Hewlett-Packard 5930A or Varian M-44 spectrometers. EI=Electron Impact, CI=Chemical Ionization, DCI=Desorption Chemical Ionization.

For the photosensitized oxygenations, a Sylvania 500T 3Q/Cl/U 200 V lamp and a typical immersion unit were used.

Synthesis of the Heterocyclic Steroids. *N*-Methyl-4-aza-5-androsten-3,17-dione (6). To a solution of **4** (5.853 g, 20 mmol) in *t*-BuOH (1.5 L), an oxidizing von Rudloff solution (24.8 g $NaIO_4$, 5.96 g K_2CO_3, 0.789 g $KMnO_4$, 1.5 L H_2O) was added, and the mixture was stirred for 2 h at r.t. The *t*-BuOH was evaporated in vacuo, HCl (10%, 60 mL) added and the resulting mixture worked up with EtOAc in the usual way. SiO_2 filtration (benzene-EtOAc 1:1) yielded 5.108 g (81.5%) of 5,17-dioxo-A-nor-3,5-secoandrostan-3-oic acid (**5**). IR (film) 3400—2500 (br), 1745, 1725, 1710. ^{1}H NMR: 0.95 (s, H_3C(18)), 1.16 (s, H_3C(19)), 9.68 (br, H-OOC(3), disappears on D_2O addition). MS 306 (M^+).

One hundred mL of a 1.5% solution of Na in EtOH, were added to 1.854 g of methylamine hydrochloride in 22 mL EtOH. After filtration, a solution of **5** (1.119 g, 4 mmol) in EtOH (54 mL) was added and the mixture was heated at 140 °C in a sealed tube, for 15 h. After allowing it to cool to r.t. and evaporation in vacuo, it was worked up with chloroform. SiO_2 chromatography (benzene-EtOAc 1:1) yielded 848 mg (80%) of pure **6**. Mp 162—167.5 °C (d) after three crystallizations. IR: 3040, 1730, 1660, 1635. UV: 235 (13800). ^{1}H NMR: 0.91 (s, H_3C(18)), 1.09 (s, H_3C(19)), 3.10 (s, H_3C-N(4)), 5.03 (dd, J_1=4.5, J_2=2, H-C(6)). MS 301 (M^+). Found: C; 75.46, H; 9.05; N 4.57%. Calcd for $C_{19}H_{27}NO_2$ (301.43): C 75.71; H 9.03; N 4.65%.

***N*-Methyl-6-methoxy-4-aza-5-androsten-3,17-dione (9).** To a solution of **7** (0.301 g, 0.8 mmol) in *t*-BuOH (120 mL), an oxidizing von Rudloff solution (2.0 g $NaIO_4$, 0.6 g K_2CO_3, 0.02 g $KMnO_4$, 450 mL H_2O) was added, and the mixture was stirred for 3 h at r.t. The *t*-BuOH was evaporated in vacuo, HCl (2M (1 M=1 mol dm^{-3}), till pH 2) was added and the resulting mixture was worked up with EtOAc to yield 0.251 g (79%) of 6β-methoxy-A-nor-3,5-seco-5,17-dioxoandrostan-3-oic acid (**8**). IR (film) 3600—2500 (br), 1750, 1715, 1100. ^{1}H NMR 0.93 (s, H_3C(18)); 1.26 (s, H_3C(19)); 3.30 (s, CH_3-O (6)); 3.58 (t, J_1=J_2=2, H-C(6)); 8.65 (br, H-OOC(3), disappears on D_2O addition).

Liquid methylamine was added in excess to a solution of **8** (0.120 g, 0.3 mmol) in THF (50 mL), and the mixture was heated at 140 °C in a sealed tube for 15 h. After allowing it to cool to r.t., it was worked up with chloroform. SiO_2 chromatography (EtOAc-cyclohexane 2:1) yielded 53 mg (51%) of **9**. IR (film) 2840, 1730, 1670—1645 (br). UV 243 (9900). ^{1}H NMR 0.96 (s, H_3C(18)), 1.05 (s, H_3C(19)), 3.15 (s, H_3C-N(4)), 3.53 (s, CH_3O(6)). MS 331 (M^+). The compound decomposed during the recrystallization procedure, which prevented its elemental analysis.

***N*-Methyl-4-aza-5-androsten-17β-ol (11).** 1.2 g $LiAlH_4$ in 120 mL dry Et_2O were placed in the round-bottom flask of a Soxhlet apparatus, and 0.400 g (1.3 mmol) of **10** were placed in its cartridge. Reflux of ether slowly added **10** on the reducing agent. After 13 h reflux and 6 h at r.t. with stirring, 6 mL of a saturated Na_2SO_4 solution were added dropwise. After filtration it was worked up with ether to yield 0.353 g (93%) of **11**. Mp 161—164 °C after three crystallizations. IR: 3450, 3075, 1645. UV 218 (5400). MS 289 (M^+). Found: C, 78.79; H, 10.82; N, 4.71%. Calcd for $C_{19}H_{31}NO$ (289.47): C, 78.84; H, 10.79; N, 4.84%.

Photooxygenation Reactions. Photooxygenation of 6. A solution of **6** (680 mg, 2.2 mmol) in dry benzene (15 mL), together with Rose Bengal-SiO_2 (701 mg), was irradiated for 20 min at 5 °C under a current of O_2. After filtration, the solution was concentrated to 10 mL with a N_2 current and immediately SiO_2 chromatographed (benzene-EtOAc 3:2) to yield 316 mg (43%) of *N*-methyl-3,5,17-trioxo-4-aza-5,6-secoandrostan-6-al (**12**), as an oil. IR 2740, 1750, 1725, 1670. UV 214 (9600). ^{1}H NMR 0.95 (s, H_3C(18)), 1.32 (s, H_3C(19)), 2.61 (d, J=6, H_2-C(7)), 3.11 (s, H_3C-N(4)), 9.66 (br s, HCO(6)), sharpens when irradiating at 2.61). MS 333 (M^+).

Jones Oxidation of 12. To a solution of **12** (84 mg, 0.25 mmol) in acetone (25 mL), 1.5 mL of Jones reagent were added, till persistence of a red color. MeOH was then added (15 mL) till green coloration and, after evaporation in vacuo, the mixture was worked up with EtOAc, to yield 86 mg (98%) of *N*-methyl-3,5,17-trioxo-4-aza-5,6-secoandrostan-6-oic acid (**13**). IR (film) 3600—2500 (br), 1750—1720 (br), 1670. ^{1}H NMR 0.89 (s, H_3C(18)), 1.30 (s, H_3C(19)), 2.60 (d, J=5, H_2-C(7)), 3.10 (s, H_3CN(4)), 7.27 (br, H-OOC(6), disappears on D_2O addition). MS 349 (M^+).

Esterification of 13. A solution of 80 mg (0.23 mmol) of **13** in 50 mL ether was treated with an ethereal solution of diazomethane. Solvent elimination in vacuo yielded 77 mg (96%) of methyl *N*-methyl-3,5,17-trioxo-4-aza-5,6-secoandrostan-6-oate (**14**). IR (film) 1745—1720 (br), 1670, 1165. ^{1}H NMR 0.93 (s, H_3C(18)), 1.37 (s, H_3C(19)); 2.61 (d, J=5, H_2-C(7)), 3.13 (s, H_3C-N(4)), 3.69 (s, H_3C-OOC(6)). MS 363 (M^+). Decomposition during recrystallization prevented its elemental analysis.

Photooxygenation of 9. A solution of **9** (23 mg, 0.07 mmol) in dry benzene (10 mL), together with Rose Bengal-SiO_2 (25 mg), was irradiated for 1 h under a current of O_2. After filtration, it was left at r.t. for 3 d. SiO_2 chromatography (EtOAc-cyclohexane 1:1) yielded 10 mg (39%) of **14** (mixed TLC, IR, ^{1}H NMR, and MS).

Photooxygenation of 11. A solution of **11** (260 mg, 0.9 mmol) in dry benzene (100 mL) and Sensitox (200 mg), was irradiated for 50 min at 5 °C and under a current of O_2. Filtration, evaporation with a current of N_2 and SiO_2 chro-

matography yielded mostly decomposition products and 58 mg (20%) of assumed *N*-methyl-5ξ,17ξ-dihydroxy-4-aza-androstan-6-one (**15**), as an oil. IR (film) 3500, 1710. ^{1}H NMR 0.65 (s, H_3C(18)), 0.70 (s, H_3C(19)), 1.92 (s, H_3C-N(4)), 2.2 (br, HO-C(17), simplifies after D_2O addition), 2.3—2.6 (m, H_2-C(3)+H_2-C(7)), 3.80 (m, HO-C(5)+HC(17), simplifies after D_2O addition). MS: EI 321 (M^+), 303(M^+ −18); CI 304 (M^++1−18); DCI 322(M^++1).

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