erhitzt. Nach dem Abkühlen wurde mit 800 ml Dichloräthan verdünnt, mit Wasser und wässeriger Natriumcarbonatlösung gewaschen, über wasserfreiem Natriumcarbonat getrocknet, eingedampft und an Kieselgel chromatographisch gereinigt. Die durch Dichloräthan/Diäthyläther 3:2 eluierten blauen Fraktionen wurden eingedampft und der Rückstand durch Einengen einer Lösung in Dichlormethan/Ligroin umkristallisiert. Das Dünnschichtchromatogramm zeigt neben einer blauen Hauptzone eine zweite blaue Zone geringer Intensität, Smp. 190–195° (Zers.). Ausbeute 0,199 g (22%).

$C_{24}H_{20}N_2O_3$ mit 20 Mol.-% H_2O	Ber.	C 74,28	H 5,30	O 13,19	Cl 0,00%
(388,04)	Gef.	,, 73,97	,, 5,63	,, 13,17	,, 0,23%

^{1}H-NMR. (100 MHz, $CDCl_3$): 2,33 (*s*, H_3C—C(3)); 2,43 (*s*, H_3C—C(2)); 2,63 (*s*, H_3C—C(6)); 4,40 (J = 11/5, *d* × *d*, H_2C—C(14)); 4,70 (J = 11/7, *d* × *d*, H_2C—C(14)); 6,45 (*s*, H—C(7)); 7,36 (J = 7/5, *d* × *d*, H—C(14)); 7,47 (*s*, H—C(1)); 7,55 (*s*, H—C(4)); 7,6–7,8 (*m*, H—C(10), H—C(11)); 8,0–8,2 (*m*, H—C(9), H—C(12)). – UV./VIS. (DMF): 645 (3400), 309 (11400).

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277. Photochemical Reactions. IV [1]. Irradiation of 17β-Acetoxy-4-aza-androst-5-en-3-one with UV.-light[1]

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(6. X. 75)

Summary. The photochemical behaviour of the title compound (**7**) is described. The obtained results indicate the high reactivity of the enamidic Δ^5 double bond.

The study of the photochemical behaviour of the unsaturated lactam function, has received relatively little attention. Monocyclic [2] and bicyclic [3] compounds yield mainly products which are the result of fragmentation and, sometimes [2b], dimerization processes. In the steroid field, the unsaturated A-homo lactams, with direct conjugation between the olefinic bond and the carbonyl group, yield again dimers [1] [4]. On the other hand, the UV.-irradiation of the steroidal enamides **1**, **2**

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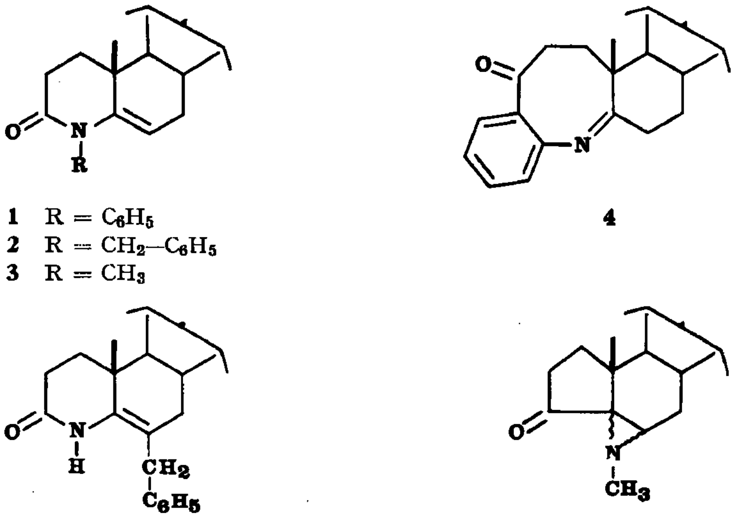
and **3**, gives the photoproducts **4**, **5**, and **6** respectively (*Scheme 1*) [5], showing the photochemical change remarkably dependent on the nature of the substituent R at the nitrogen atom.

Scheme 1



1 R = C_6H_5
2 R = $CH_2—C_6H_5$
3 R = CH_3

4

5

6

These results impelled us to investigate the behaviour, under similar photochemical conditions, of the corresponding, N-unsubstituted enamide **7**, which can be easily obtained from testosterone acetate [6].

The irradiation of a benzene (*Merck*, analytical purity) solution of **7**, with the light of a low pressure Hg lamp, under N_2 atmosphere, during 22 h, yielded a mixture of starting material **7** (25%), phenyl derivative **8**2) (3%), hydroxy compound **9**3) (22%) and the diol **10** (25%) (*Scheme 2*).

When the reaction was carried out in the presence of D_2O, the same mixture of compounds was obtained, observing incorporation of deuterium in the aromatic ring of the phenyl derivative (**11**)4) and in position C_6 of the water addition product (**12**) and of the recovered starting material (**13**)5).

This result points to the participation of the water present in the reaction medium, in the formation of **8**, and to the thermal unstability of **9**, which easily dehydrates to **7**6), increasing the proportion of starting material apparently unreacted.

We are grateful to PD Dr. *H. Wehrli*, Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule, Zürich, for kindly supplying of starting material, for his help in recording of spectra, as well as for many stimulating discussions during the work. One of us (J. B.) also thanks the *Plan de Formación de Personal Investigador, del Ministero de Educacion y Ciencia, Madrid*, for a doctoral fellowship.

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2) The NMR.-, IR.-, UV.- and mass spectra of the new compounds, are in good agreement with the proposed structures and will be reported in the experimental part of this work.

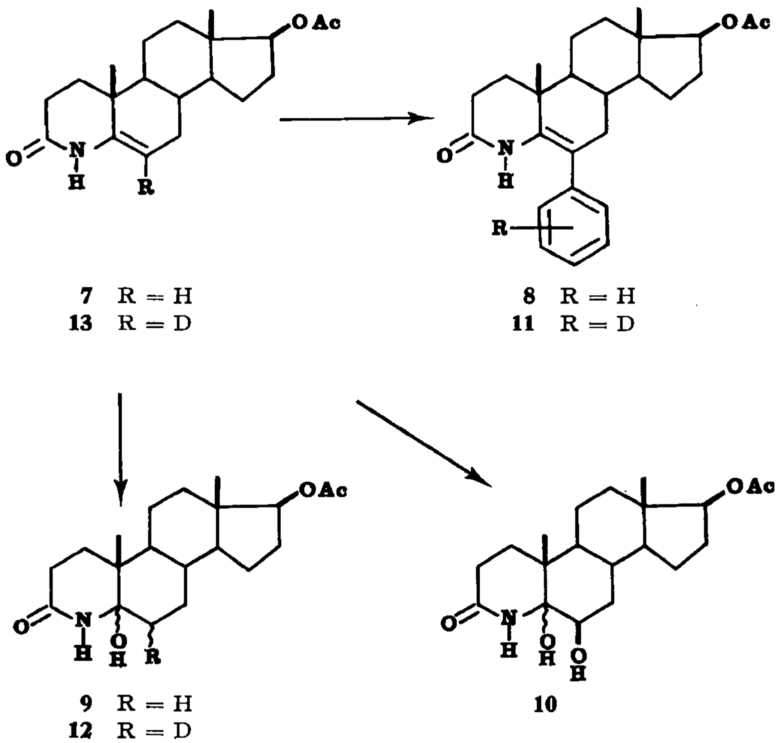
3) Product **9** is the result of water addition to the Δ^5 double bond of **7**, the water originating from the solvent (approx. water contents = 0.03%).

4) See mass spectra of **8** and **11** in the experimental part.

5) See NMR.- and mass spectra in the experimental part.

6) **9**, when heated in benzene or acetone, yields quantitatively **7** (see experimental part).

Scheme 2



7 R = H
13 R = D

8 R = H
11 R = D

9 R = H
12 R = D

10

Experimental Part

For general remarks see [7]. The irradiations were carried out at room temperature, under N_2-atmosphere with a low pressure Hg lamp (NK 6/20, *Quarzlampen GmbH*, Hanau), disposed in a typical immersion unit. Crystallizations are from acetone/petrol ether (b.p. 50–70°).

UV.-irradiation of **7**. – a) *In benzene*. A solution of 550 mg **7** in 500 ml benzene (Merck, analytical purity) was irradiated during 22 h. Solvent evaporation *in vacuo* and at room temp. yielded 670 mg of a yellowish amorphous solid, mixture of several components. Chromatography of this material with benzene/chloroform/methanol/triethylamine 16:4:2:1, furnished three main fractions. The first fraction was a mixture of compounds **7** and **8**, which could be separated into its components after a second chromatography (see further down). The second fraction consisted of 144 mg of *17β-acetoxy-5ξ-hydroxy-4-aza-androstan-3-one* (**9**), m.p., after three crystallizations, 290–292° (dec.). – IR.: 3400, 3270, 1735, 1640, 1620, 1250. – UV.: end absorption. – NMR.: 0.92, *s*, $H_3C(18)$; 1.09, *s*, $H_3C(19)$; 2.09, *s*, C(17)—$OCOCH_3$; 4.20, br.; HO—C(5); 4.60, *m*, H—C(17); 6.96, br.; NH (after D_2O addition the signals at 4.20 and 6.96 vanished). – MS.: 331 (M^+ – 18).

$C_{20}H_{31}NO_4$ (349.46) Calc. C 68.74 H 8.94 N 4.01% Found C 68.85 H 9.19 N 3.69%

The third and last fraction, was a mixture of **9** and **10**, which also could be separated into its compounds, after a new chromatography (see afterwards).

As stated above, through a second chromatography of the first fraction, with benzene/ethyl acetate 1:1, the mixture of **7** and **8** was separated. First, 23 mg of 17β-acetoxy-6-phenyl-4-aza-androst-5-en-3-one (**8**) were eluted, m.p. 247–249° (two crystallizations). – IR.: 3400, 1730, 1680, 1490, 1250, 765, 705. – UV.: 243 (7.700). – NMR.: 0.88, *s*, $H_3C(18)$; 1.20, *s*, $H_3C(19)$; 2.08, *s*, C(17)—$OCOCH_3$; 4.62, *m*, H—C(17); 6.90–7.40, *m*, $C_6H_5(6)$ + NH. – MS.: 407 (M^+), other fragments of interest: 392 ($M^+ - CH_3$), 374 ($M^+ - CH_3CO$), 330 ($M^+ - C_6H_5$), 316 ($M^+ - C_7H_7$).

$C_{26}H_{33}NO_3$ (407.52) Calc. C 76.62 H 8.16 N 3.44% Found C 76.54 H 7.96 N 3.40%

Then, 169 mg of pure starting material **7** [6] were isolated (identification through mixed melting point, IR.-spectrum and TLC.).

The rechromatography of the third fraction in benzene/chloroform/methanol/triethylamine 16:4:0.5:0.5 furnished further 12 mg of the hydroxy derivative **9** (identification through mixed m.p., IR.-spectrum and TLC.) and 164 mg of *17β-acetoxy-5ξ,6β-dihydroxy-4-aza-androstan-3-one* (**10**), m.p. 175–177° (after three crystallizations). – IR.: 3485, 3400, 3300, 3210, 1735, 1660, 1645, 1255. – UV.: end absorption. – NMR. (CD_3OD): 0.88, *s*, $H_3C(18)$; 1.20, *s*, $H_3C(19)$; 2.07, *s*, C(17)–$OCOCH_3$; 3.66, *t*, $J = 3$, H–C(6); 4.63, *m*, H–C(17). – MS.: 365 (M^+).

$C_{20}H_{31}NO_5$ (365.46) Calc. C 65.73 H 8.55 N 3.83% Found C 65.58 H 8.70 N 3.58%

b) *In D_2O-saturated benzene.* A solution of 624 mg **7** in 500 ml D_2O-saturated benzene (after distilling 3 ml from the mentioned solution, 0.5 ml D_2O were added and the distillation continued till a total of 6 ml; further 0.5 ml D_2O were then added and the solution cooled to room temp.), was irradiated during 21 h. Solvent evaporation *in vacuo* and at room temp. yield again a yellowish amorphous mixture of several components (714 mg). Its chromatography, using this time the following gradient: benzene/chloroform/methanol/triethylamine 16:4:0:0.1; 16:4:0.5:1; 16:4:0.2:0.1; 16:4:2:1, furnished 54 mg of impure **8** (**11**), which was further purified by means of a new chromatography with benzene/ethyl acetate 1:1, to yield 28 mg of pure compound (identification through mixed m.p., TLC., IR.-, NMR.- and mass spectra: 408 (M^+), other fragments of interest: 393 ($M^+ - CH_3$), 365 ($M^+ - CH_3CO$), 330 ($M^+ - C_6H_4D$), 316 ($M^+ - C_7H_6D$). A second fraction afforded 234 mg of starting material **7** (**13**) (identification through mixed m.p., TLC., IR.-, NMR.- and mass spectra. – NMR.: 0.85, *s*, $H_3C(18)$; 1.12, *s*, $H_3C(19)$; 2.08, *s*, C(17)–$OCOCH_3$; 4.62, *m*, H–C(17); 4.86, *d*×*d*, $J_{6,7} = 4$, $J_{6,7'} = 2$, H–C(6); 8.39, br., NH; the integral value at 4.86 is 0.3, which indicates 70% incorporation of deuterium, corroborated by the MS.: $M^+ = 332$ and 331). At last, a third fraction containing **9** (**12**)+**10**, was rechromatographed with benzene/chloroform/methanol/triethylamine 16:4:0.5:0.5, yielding 142 mg of **9** (**12**) (identified through mixed m.p., TLC., IR.-, NMR.- and mass spectra: 332 ($M^+ - 18$) and 139 mg of **10** (identification through mixed m.p., IR.- and mass spectra: 365 (M^+).

Dehydration of **9**. – a) *In boiling acetone.* 19 mg **9** were heated in 10 ml acetone, during 7 h, under refluxing. Solvent evaporation *in vacuo*, yielded quantitatively **7** (identification, after two crystallizations, through mixed m.p., TLC. and IR.).

b) *In boiling benzene.* 60 mg **9** were heated in 20 ml benzene, during 30 min, under refluxing. Solvent evaporation *in vacuo*, yielded 58 mg **7** (identification, after two crystallizations, through mixed m.p., TLC. and IR.).

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