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Photoreaction of *D*-Nor-5*α*-androstan-16-one Oxime, a Steroidal Cyclobutanone Oxime[1)]

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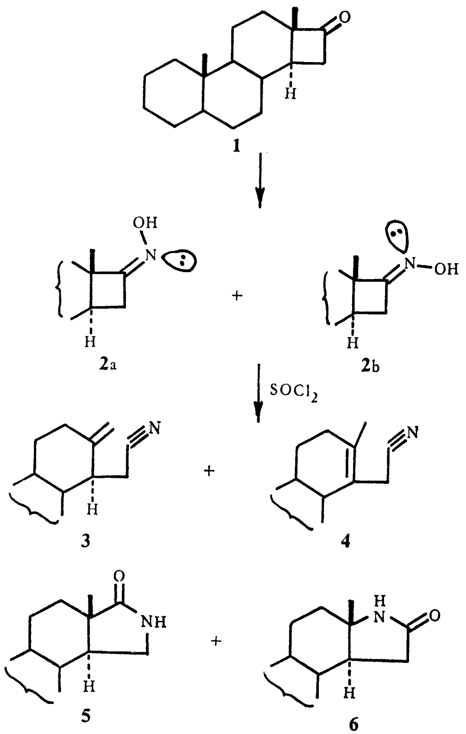
Irradiation of *D*-nor-5α-androstan-16-one oxime in methanol leads to a mixture of seco-nitriles; *D*-nor-13,16-seco-5α-androst-13(18)-ene-16-nitrile (**3**), *D*-nor-13,16-seco-5α-androst-12-ene-16-nitrile (**7**), 13ξ-methoxy-*D*-nor-13,16-seco-5α-androstane-16-nitrile (**8**), and 15-hydroxy-*D*-nor-15,16-seco-5α-androstane-16-nitrile (**9**). These result from ionic α-fissions at either of the α-bonds. Low yields of three lactams, 17-aza-5α-androstan-16-one (**6**), 17-aza-5α,13α-androstan-16-one (**11**), and 16-aza-5α-androstan-17-one (**5**), resulting from photo-Beckmann rearrangement, are also formed. The formation of **11** is the second proven example of a photo-Beckmann rearrangement in which a chirality of the migrating carbon center is not retained in the product lactam and an intervention of a ring-opened intermediate must be involved. It was found that direction of the α-cleavage of this excited four-membered cyclic ketone oxime was not governed only by the stability of cleaved ions, since seco-nitrile **9** resulting from α-fission to a less stable primary carbonium ion was formed together with seco-nitriles **3**, **7**, and **8** from a more stable tertiary carbonium ion. The Beckmann rearrangement of the mixture of *syn* and *anti* oximes with thionyl chloride afforded the two expected lactams **5** and **6** together with the products of Beckmann fission **3** and *D*-nor-13,16-seco-5α-androst-13(14)-ene-16-nitrile resulting from a cleavage to tertiary carbonium ion.

In the photo-Beckmann rearrangement of steroidal saturated ketone oximes, the chirality of the migrating center of the oximes is generally retained in the product lactams.[2)] We have found one exception to this rule: irradiation of *O*-acetylandrosterone oxime afforded a pair of lactams epimeric at the C-13.[3)] This exception implies that another mechanism, in which lactams are formed *via* rebonding of species resulting from α-fission of the oximes or the corresponding species resulting from the breakdown of the intermediate oxaziridines, is involved in the lactam formation. In order to gain more insight into the mechanism of the photoreaction of oximes, the Beckmann and the photo-Beckmann rearrangements of a steroidal cyclobutanone oxime were investigated. The results are described in this paper.

Results

D-Nor-5α-androstan-16-one oxime (**2**), prepared by the standard method, was chosen as the substrate. NMR showed that the crude oxime, as well as the one recrystallized from aqueous ethanol, were mixtures of the (*Z*) and (*E*) isomers **2a** and **2b**. Thus, a signal due to the 18-H of the oxime before the recrystallization appeared as two singlets at τ 8.87 and 8.84 (19-H as a singlet at τ 9.22), indicating it to be a mixture of geometrical isomers. This was proved more clearly by an analysis of the signals in lower fields. In the spectrum, there were a triplet centered at τ 7.34 with J=11.3 Hz, a double doublet centered at τ 7.15 with J=7.8 and 11.3 Hz, and another double doublet centered at τ 6.54 with J=7.8 and 11.3 Hz. The integrated signal areas corresponded to 1 H, 0.8 H and 0.2 H. These signals were ascribable to the 15α(or β)-H of **2a** and **2b**, the 15β(or α)-H of **2a** and the 15β(or α)-H of **2b**. As we reported previously, protons of the hydroxyimino group, which is nearly eclipsed by the C=N bond of the oximes, are deshielded[2)] when the hydroxyl group is *syn* to them and appear at *ca.* τ 6.6. The α-oriented proton at the C-15 of **2b** falls in this category; from the ratio of the signal areas of the 15β(or α)-H of **2a** and the 15β(or α)-H of **2b**, the ratio of **2a** and **2b** is estimated to be approximately 4: 1. This ratio did not change significantly after its recrystallization from aq ethanol.



Scheme 1.

Scheme 1 shows the results of ordinary Beckmann rearrangement. Treatment of oxime mixture **2a** and **2b** with thionyl chloride at room temperature afforded a product mixture, much simpler than that from the photolysis (*vide infra*). The mixture was subjected to preparative TLC to afford a mixture of two seco-nitriles **3** and **4** and a mixture of two lactams **5** and **6**. The two seco-nitriles **3** and **4** were separated by preparative TLC with silica gel containing silver nitrate. The structure of the less mobile compound **3**, mp 66—70

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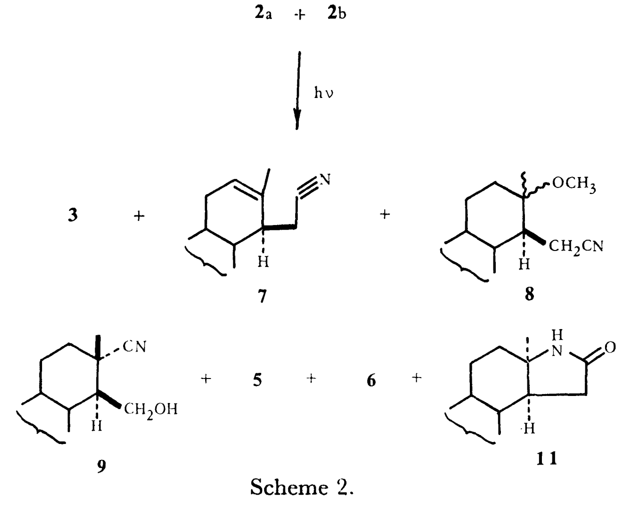
°C, (35%) was confirmed to be *D*-nor-13,16-seco-5α-androst-13(18)-ene-16-nitrile (**3**) by IR, mass, and NMR spectroscopy. The molecular formula $C_{18}H_{27}N$ was confirmed by high resolution mass spectrometry. The IR spectrum exhibits a band due to the C≡N group at 2242 cm^{-1} and a series of bands due to the *exo*-methylene at 1647 and 894 cm^{-1}. The low resolution mass spectrum shows the molecular ion at *m/e* 257 (71.2%), $M^{+}-CH_3$ at *m/e* 242 (57.0%), the base peak at *m/e* 149, and the ion at *m/e* 109 (63.1%). The NMR spectrum has a singlet due to the 19-H at τ 9.28 and no signal due to the 13β-methyl group is found. Instead, the spectrum shows two broad one-proton singlets at τ 5.16 and 5.28($W_{1/2}$=4.5 Hz) and a two-proton doublet centered at τ 7.38 (J=5.3 Hz). These results are in agreement with the structure **3**; the two broad singlets are ascribed to the *exo*-methylene protons and the doublet to the C-15 methylene protons.

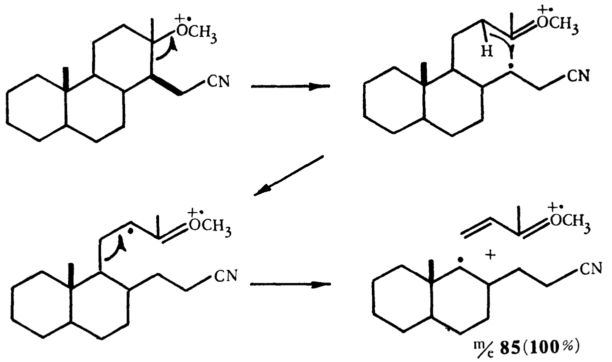
The spectral results of oily seco-nitrile **4** (8%) were in agreement with the structure of *D*-nor-13,16-seco-5α-androst-13(14)-ene-16-nitrile (**4**). The high resolution mass spectrometry proved that **4** has the molecular formula $C_{18}H_{27}N$. The low resolution mass spectrum of **4** exhibits the molecular ion at *m/e* 257 (15.7%), $M^{+}-CH_3$ peak at *m/e* 242 (5.6%), a fragment at *m/e* 149 (5.1%), and the base peak at *m/e* 109. The IR spectrum has a nitrile band at 2245 cm^{-1}. The NMR spectrum has two singlets (each 3H) at τ 9.28 and 8.32 and a two-proton singlet at τ 6.93. These signals are assignable to the 19-H, the 18-H, and the 15-H of **4**.

Lactams **5** and **6**, obtained from a less mobile fraction, were separated with the aid of HPLC. The molecular formula of lactam **5** (12%) which has a shorter retention time was confirmed to be $C_{18}H_{29}NO$ by high resolution mass spectrometry. The physical and the spectral properties were in agreement with 16-azaandrostan-17-one (**5**).[4] The molecular formula of lactam **6** (7%) which has a longer retention time, was also confirmed to be $C_{18}H_{29}NO$ by high resolution mass spectrometry. The physical and spectral properties were in accordance with 17-azaandrostan-16-one (**6**).[4]

The photo-Beckmann rearrangement of oxime **2** in methanol was carried out under the same procedure as we reported previously.[2] Irradiation of a solution of the mixture of oximes **2a** and **2b** afforded a complex mixture of the products, from which a mixture of seco-nitriles **3** and **7**, two other seco-nitriles **8** and **9**, and three lactams **5**, **6**, and **11** have been isolated by preparative TLC (Scheme 2). Although the separation of the mixture of seco-nitriles **3** and **7** to its components by means of preparative TLC was unsuccessful, spectrometry confirmed that it was a mixture of two seco-nitriles, **3** and *D*-nor-13,16-seco-5α-androst-12-ene-16-nitrile (**7**). Thus, the IR spectrum shows the molecular ion at *m/e* 257. The NMR shows all the signals due to seco-nitrile **3** obtained by the Beckmann rearrangement. Besides these signals it has two singlets at τ 9.29 and 8.34, and a broad singlet at τ 4.34. These signals are ascribed to the 19-H, the 18-H, and the 12-H of *D*-nor-13,16-seco-5α-androst-12-ene-16-nitrile (**7**). On the basis of the ratio of the integrated areas of the singlet at τ 4.34 due to the 12-H of **7** and the two singlets at τ 5.16 and 5.28 due to the *exo*-methylene protons of **3**, the ratio of **3** and **7** was estimated to be approximately 1.8 : 1.0 (2.8% and 1.5% yields). The structure of a less mobile amorphous compound (**8**) (1%) was proved to be 13ξ-methoxy-*D*-nor-13,16-seco-5α-androstane-16-nitrile by means of spectrometry. The IR spectrum shows a nitrile band at 2192 cm^{-1}. The high resolution mass spectrum of **8** proves that it has the molecular formula $C_{19}H_{31}NO$. The NMR exhibits three singlets (each 3H) at τ 9.23, 8.84, and 6.80, and a doublet (2H) centered at τ 7.84 (J=3.0 Hz). These signals are ascribable to the 19-H, the 18-H, the methoxyl group and the 15-H of **8**. The fragment ions in the mass spectrum supported this assignment. In the spectrum the base peak is present at *m/e* 85 and no other peak has an abundance of more than 7.9%. The formation of the base peak is rationalized in terms of structure **8** in a manner depicted in Scheme 3. The other crystalline compound (**9**) (2.7%) was also a seco-nitrile and its structure, 15-hydroxy-*D*-nor-15,16-seco-5α-androstane-16-nitrile (**9**), has been assigned from the analysis of the mass, IR, and NMR spectra. The molecular formula $C_{18}H_{29}NO$ was deduced from high resolution mass spectrometry. The IR spectrum exhibits a nitrile band at 2220 cm^{-1} and a hydroxyl band at 3571 cm^{-1}. The NMR shows two singlets (each 3H) at τ 9.27 and 8.24 and a doublet (2H) centered at τ 6.06 (J=2 Hz) which are ascribed to the 19-H, the 18-H, and the 15-H of **9**. The low resolution mass spectrum exhibits the parent

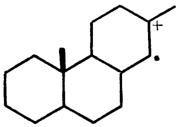


Scheme 2.



Scheme 3.

peak at *m/e* 275 (58.0%), M^+-CH_3 at *m/e* 260 (40.8%), M^+-H_2O at *m/e* 257 (25.6%), M^+-CH_2OH at *m/e* 244 (38.3%), and a base peak at *m/e* 218. Structure **10** is assigned to the last fragment ion.



m/e 218(100%)

10

A mixture of lactams, which were again difficult to separate by means of preparative TLC, was obtained as a less mobile fraction. This mixture could be separated, however, to 16-aza-5α-androstan-17-one (**5**), 17-aza-5α-androstan-16-one (**6**), and a new lactam **11** by HPLC. Lactams **5** and **6** were identified by direct comparisons with the authentic specimens obtained by the Beckmann rearrangement. The new lactam **11** has the molecular formula $C_{18}H_{29}NO$, as shown by its high resolution mass spectrum, and the lactam carbonyl bands at 1701 and 1675 cm^{-1} and the NH band at 3240 cm^{-1} in the IR spectrum. The most diagnostic spectral property is the mass spectrum which shows a fragmentation pattern nearly identical to that of 17-aza-5α-androstan-16-one (**6**). Thus, the structure of the new lactam is clearly 17-aza-5α,13α-androstan-16-one (**11**).

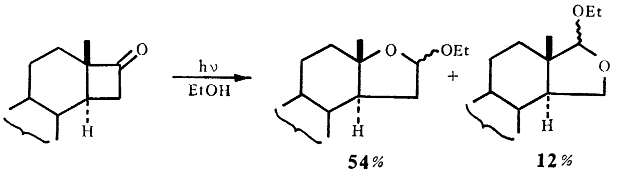
Discussion

These results confirmed that the photo-reaction of fused cyclobutanone oxime **2** leads mostly to the products resulting from α-fissions and gives only a low yield of a mixture of lactams. Although the yield of lactams is very low, the present result is the second proven example of a photo-Beckmann rearrangement in which the chirality of the migrating center of the oximes is not retained in the product lactam. The formation of lactam **11** implies that, as we described in our previous papers,[2,3] a ring-opened intermediary species should be involved in the course of the photo-rearrangement and reinforces the possibility of the presence of an exceptional mechanistic pathway for the lactam formation from the excited saturated ketone oxime.

As we pointed out in our previous papers, the α-fission reaction is rare in the photo-reaction of oximes.[7] The oximes in which α-fissions in the photo-reaction are observed[8,9] appear to be those in which an increase of non-bonded interaction or strain in the molecule is expected by the formation of the corresponding oxaziridine intermediate.

The observed α-fission in the present case is attributable to the ring strain of the four-membered ring. The present α-fission is apparently ionic in nature since all the products which result from α-fission are those expected for an ionic mechanism. Another example of ionic α-fission was recently reported by Inamoto and his colleagues.[9]

A remarkable feature in the present photo-reaction is the formation of nitrile **9** which arises from a less stable primary carbonium ion generated by a cleavage of the C-15–C-16 bond. This is contrasted to the α-fission in the ground state reaction in which the products in α-fission are nitriles **3** and **4** resulting from a more stable carbonium ion, as would be expected. This result indicates clearly the difference in behaviour of the α-fission in the ground state reaction and in the excited state reaction. The selectivity in the site of the α-fission in excited cyclobutanone oxime **2** seems to be reduced. An analogous anomalous behaviour for the α-fission has been found in an excited steroidal cyclobutanone; 3β-methoxy-*D*-nor-5α-androstan-16-one gives 12% of the acetal derived from a less stable 1,4-biradical.[10,11] (Scheme 4).



Scheme 4.

It is noted that while the photo-Beckmann rearrangement of *O*-acetylandrosterone oxime, a *trans* fused cyclopentanone oxime, afforded two isomeric lactams arising from the migration of the more-substituted carbon center and no accompanying lactams arising from the migration of the less-substituted carbon center,[3] the corresponding *trans* fused cyclobutanone oxime **2** afforded lactam **5** arising from the migration of the less substituted carbon center.

Experimental

Mps were determined with a Yanagimoto micro-melting point apparatus. IR spectra were determined for Nujol mulls with a JASCO IR-E spectrophotometer unless stated otherwise. 100 MHz ^1H NMR spectra were recorded with a JEOL PS 100 high-resolution spectrometer (solvent $CDCl_3$; Me_4Si as internal reference). Preparative TLC was carried out on Wakogel B-5F unless stated otherwise. Mass spectra were recorded in the Faculty of Pharmaceutical Sciences or the Faculty of Agriculture of this University with a Hitachi JMS-D 300 spectrometer using a direct inlet system. (Ion source temperatures: 175 °C for compounds **2, 3,** and **8**; 180 °C for compounds **6** and **9**; 185 °C for compound **5** and 100 °C for compound **4**. Ionizing voltage, 70 eV). Only fragment peaks of relative intensities over 40% are mentioned. High resolution mass spectra were measured by Miss Y. Chiba in the Faculty of Agriculture. Dotite spectrosol methanol (Wako) was used as solvent for the photoreactions.

Preparation of D-*Nor-5α-androstan-16-one Oxime **2a** and **2b**.* *D*-Nor-5α-androstan-16-one (**1**) (50 mg), hydroxylamine hydrochloride (30 mg) and sodium acetate trihydrate (20 mg) in ethyl alcohol (1 ml) and water (0.2 ml) were stirred for 2 h at room temperature. After the usual work-up the product was recrystallized from aq ethanol to afford the oxime (15 mg), mp 87—90 °C, which was a mixture of geometrical isomers. Found: C, 78.31; H, 10.42; N, 5.30%. Calcd for $C_{18}H_{29}NO$: C, 78.49; H, 10.61; N, 5.09%. IR: 3260 (OH), 1705 (C=N), and 937 cm^{-1}. MS *m/e* (rel intensity) 275 (M^+, 11.7), 260 (M^+-CH_3, 39.8), 259 (M^+-16, 22.5), 258 (M^+-H_2O, 100), 109 (76.6), 95 (63.9), 81 (59.1), 67 (68.3), 55 (68.2), 41 (60.7); for NMR see text.

The Beckmann Rearrangement of D-*Nor-5α-androstan-16-one Oxime, **2a** and **2b**.* To the amorphous oxime (41 mg) in dioxane (2 ml) was added thionyl chloride (0.5 ml) at room temperature. The solution was stirred for 20 min. The solution was extracted with dichloromethane. The organic layer was washed with water, 5% sodium hydrogencarbonate, and water again and then dried (Na_2SO_4). The residue(40 mg) was subjected to preparative TLC with a 2 : 1 mixture of dichloromethane and diethyl ether to afford two fractions (A and B). The more mobile fraction A (27 mg) was a mixture of the Beckmann fission products and was subjected to preparative TLC. The TLC plates were developed twice with hexane and benzene, once with a 9 : 1 mixture of hexane and benzene, and five times with a 99: 9 : 1 mixture of hexane, benzene, and dichloromethane to afford two fractions. The more mobile fraction A_1 (6 mg) was still a mixture of two nitriles **3** and **4**. This fraction was again subjected to preparative TLC (Wakogel B-5F containing 5% silver nitrate) with a 3: 1 mixture of benzene and diethyl ether to afford two fractions. The more mobile fraction (3 mg, 8%) was a colorless oil and was a 13,17-seco-nitrile **4**. Found: *m/e* 257.2124. Calcd for $C_{18}H_{27}N$: M, 257.2141; IR (Nujol): 2245 cm^{-1} (C≡N). For MS and NMR see text.

The less mobile crystalline fraction (2 mg) was the seco-nitrile **3**. The less mobile crystalline fraction A_2 (12 mg) was also nearly pure nitrile **3**, which gave crystals on addition of methanol, mp 66—70 °C. Found: *m/e* 257.2160. Calcd for $C_{18}H_{27}N$: M, 257.2141; IR (Nujol): 2242 (C≡N), 1773, 1647, and 894 cm^{-1} ($C=CH_2$); MS *m/e* (rel intensity) 257 (M^+, 71.2), 242 (M^+-CH_3, 57.0), 163 (46.6), 149 (100), 109 (63.1), 95 (60.4), 81 (68.3), 67 (59.7), 55 (64.5), and 41 (50.0). For NMR see text.

The fraction B (11 mg) was subjected to HPLC (μ Bondapak CN; JASCO UVIDEC-100 detector; pump, Varian Series 4100) with diethyl ether as the solvent. The fraction (7 mg) having the shorter retention time (7.5 min) was 16-azaandrostan-17-one (**5**). This was recrystallized from acetone to yield crystals (5 mg, 12%), mp 259—261 °C. (lit,[4] 259—260 °C). Found: *m/e* 275.2242. Calcd for $C_{18}H_{29}NO$: M,+ 275.2247; IR: 3306 (NH), 1716 and 1679 cm^{-1} (lactam carbonyl) (lit,[4] 3451, 3200, 1720, and 1700 cm^{-1}); MS *m/e* (rel intensity) (ion-source temp, 185 °C, 70 eV) 275 (M^+, 100), 260 (21.5), 230 (24.6), 218 (28.0), and 98 (33.8%) (lit,[4] *m/e* 275 (100), 260 (25), 230 (16), and 218 (26%); NMR: τ 9.04 (3H, s, 18-H), 9.22 (3H, s, 19-H), 7.01 (1H, t, 15β-H), 6.08 (1H, dd, 15α-H) ($J_{15\alpha,15\beta}=J_{15\beta,14\alpha}=9.8$ Hz; $J_{15\alpha,14\alpha}=4.5$ Hz), and 3.41 (1H, br. s, $W_{1/2}$ 12 Hz, NH).

The fraction (3 mg, 7%) of longer retention time (11.5 min) was 17-azaandrostan-16-one (**6**). This was recrystallized from acetone to yield crystals (2 mg), mp 250—251 °C. (lit,[4] mp 256—257 °C). Found: *m/e* 275.2255. Calcd for $C_{18}H_{29}NO$: M, 275.2247, IR: 3287 (NH), 1715 and 1677 cm^{-1} (lactam carbonyl) (lit,[4] 3420, 3200, 1720, and 1697 cm^{-1}); MS *m/e* (rel intensity) (ion-source temp 180 °C and ionizing voltage 70 eV) 275 (M^+, 1.2), and 260 (100%) (lit,[4] *m/e* 275 (2) and 260 (100); 8.94 (3H, s, 18-H), 9.24 (3H, s, 19-H), 7.89 (1H, d, 15α- or 15β-H), 7.91 (1-H, d, 15α- or 15β-H) ($J_{15\beta,14\alpha}=J_{15\alpha,14\alpha}=9.8$ Hz) 4.04 (1-H, br. s, $W_{1/2}$ 10 Hz).

The Photo-Beckmann Rearrangement of D-*Nor-5α-androstan-17-one Oxime.* The mixture of *syn* and *anti* oximes (300 mg) in methanol (300 ml) was irradiated for 48 h with a 15-W low pressure mercury arc. Argon was slowly bubbled during the irradiation. After the removal of the solvent, the residue was subjected to preparative TLC (Wakogel B-5F) with a 1: 4 mixture of diethyl ether and benzene to afford eight fractions A (53 mg), B (33 mg), C (21 mg), D (16 mg), E (15 mg), F (37 mg), G (24 mg), and H (80 mg) in the order of decreasing mobility. The fraction A was subjected again to preparative TLC with benzene to afford two fractions (A_1 and A_2). The fraction A_1 (34 mg) was further subjected to preparative TLC with a 5: 1 mixture of hexane and benzene. The plates were developed five times to afford a mixture of two seco-nitriles **3** and **7** (12 mg, 4.3%). Analysis of the NMR spectrum is described in the text. The fraction B was subjected to preparative TLC with benzene to afford a gummy compound (9 mg). This was again purified by preparative TLC (Merck silica gel 60 F_{254} with concentration zone) with a 4 : 1 mixture of hexane and diethyl ether to afford a colorless gum **8** (3 mg, 1%). Found: *m/e* 289.2391. Calcd for $C_{19}H_{31}NO$: M, 289.2404; IR (neat): 2192 (C≡N), 1468, 1451, 1436, 1378, 1135, and 1084 cm^{-1}; MS *m/e* (rel intensity) 289 (M^+, 3.6%), 274 (2.6), 257 (2.6), 242 (1.4), 85 (100), 72 (4.5), 67 (5.1), 55 (7.9), and 41 (5.1), for NMR see text. The fraction E was again purified by preparative TLC to afford the seco-nitrile **9** (8 mg) which was recrystallized from diethyl ether–hexane to afford crystals, mp 164—166 °C. Found: *m/e* 275.2241. Calcd for $C_{18}H_{29}NO$: M, 275.2248; IR (Nujol): 3571 (OH), 2220 (C≡N) and 1088 cm^{-1}. For NMR see text; MS *m/e* (rel intensity) (ion-source temp 180 °C, 70 eV) 275 (M^+, 58.0%), 260 (40.8), 257 (25.6), 247 (11.8), 244 (38.3), 242 (23.2), 218 (100), 200 (15.3), 190 (26.7), 175 (15.6), 149 (33.6), 135 (18.5), 121 (26.5), 110 (54.8), 109 (64.4), 95 (7.13), 81 (71.6), 67 (65.4), 55 (65.9), and 41 (62.1). The fraction F was again subjected to preparative TLC (Merck silica gel 60 F_{254} with concentration zone) with a 4 : 1 mixture of hexane and ethyl acetate. The plates were developed five times to afford two fractions (F_1 and F_2). The fraction F_1 (2 mg) was unidentified and a less mobile fraction F_2 (19 mg) was a mixture of other seco-nitriles. However, the separation to its components by preparative TLC was not successful. The fraction H was subjected to preparative HPLC, as with the case of the lactam mixture from the Beckmann rearrangement, to afford three fractions (H_1, H_2, and H_3) in the order of the retention times. The fraction H_1 (63 mg) with the shortest retention time was an unidentified gum. The second fraction H_2 (2 mg, 0.7%) was 16-aza-5α-androstan-17-one **5** identical with the specimen obtained by the Beckmann rearrangement. The fraction H_3 (8 mg, 2.7%) was a mixture of two lactams, 17-aza-5α-androstan-16-one (**6**) and 17-aza-5α,13α-androstan-16-one (**11**). This was subjected to preparative HPLC (μ Bondapak NH_2) with diethyl ether as the solvent to afford pure lactam **6** and its epimer **11** in a 3 : 1 ratio. Lactam **6** with the shorter retention time was identical with an authentic specimen of lactam **6** obtained by the Beckmann rearrangement. The new lactam **11** having a longer retention time was recrystallized from diethyl ether. It had mp 154—157 °C. Found: *m/e* 275.2249. Calcd for $C_{18}H_{29}NO$; M, 275.2249; for IR see text. NMR: τ 8.83 (3H, s, 18-H) and 9.36 (3H, s, 19-H), MS *m/e* 275 (rel intensity) (M^+, 3.9%), 260 (M^+-CH_3, 100), 136 (6.9), 109 (4.9), 81 (5.9), 79 (4.3), 67 (7.5), 55 (8.0), and 41 (8.6).

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11) This anomaly in the direction of α-fission can not be taken as general for excited cyclobutanones, since all other monocyclic cyclobutanones and 3β-methoxy-*D*-nor-5α,13α-androstan-16-one show good selectivity with respect to the site of α-cleavage. [D. R. Morton, E. Lee-Ruff, R. M. Southam, and N. J. Turro, *J. Am. Chem. Soc.*, **92**, 4349 (1970)].