846 © 1981 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 54, 846—851 (1981) [Vol. 54, No. 3

The Photo-Beckmann Rearrangement of Steroidal β,γ-Unsaturated Ketone Oximes[1]

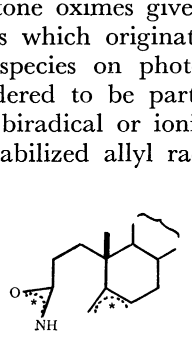
Hiroshi SUGINOME,*,** Norio MAEDA, Yuko TAKAHASHI, and Nobuyoshi MIYATA
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

(Received December 8, 1979)

The photoreaction of 4,4-dimethylcholest-5-en-3-one oxime, a β,γ-unsaturated ketone oxime, has given two lactams, 4a,4a-dimethyl-3-aza-*A*-homocholest-5-en-4-one and 4a,4a-dimethyl-4-aza-*A*-homocholest-5-en-3-one resulting from photo-Beckmann rearrangement. 4,4,6-Trimethylcholest-5-en-3-one oxime behaved analogously on photolysis, yielding two lactams but accompanied by 4,6-dimethyl-4-methylene-3,4-secocholest-5-ene-3-nitrile as a minor product. In contrast, major products in the ordinary Beckmann rearrangement are nitriles resulting from the second order Beckmann rearrangement.

Our previous studies on the photo-Beckmann rearrangement of several steroidal ketone oximes established that the chirality of the migrating group center is retained in the product lactams, indicating that the lactams are formed *via* a concerted reorganization of the intermediate oxaziridines and that the migrating group center does not become separated from the migration terminus in the course of the photo-rearrangement.[2–4] This conclusion was further supported by our recent study on the photoreaction of a β,γ-cyclopropyl ketone oxime.[5] We have found, however, that there are some exceptional cases[6] in which ionic or radical species resulting from a cleavage of a bond α to their hydroxyimino group should be considered to be involved as intermediate species in the photochemical lactam formation from oximes. Moreover, the possibility of lactam formation occurring *via* coupling of radical pairs or biradical species has been suggested for photochemical lactam formation from some fused bicyclic oxaziridines.[7]

In connection with these paths of the photochemical lactam formation, it is worth studying whether cyclic β,γ-unsaturated ketone oximes give lactams or nitriles and other products which originate from the radical pair or biradical species on photolysis. This group of oximes is considered to be particularly susceptible to the fission into biradical or ionic species by virtue of generation of stabilized allyl radicals or ions (*e.g.*, A).



(A) * radical or ion

In this paper, the results on the photoreactions of two steroidal β,γ-unsaturated ketone oximes are described.

Results and Discussion

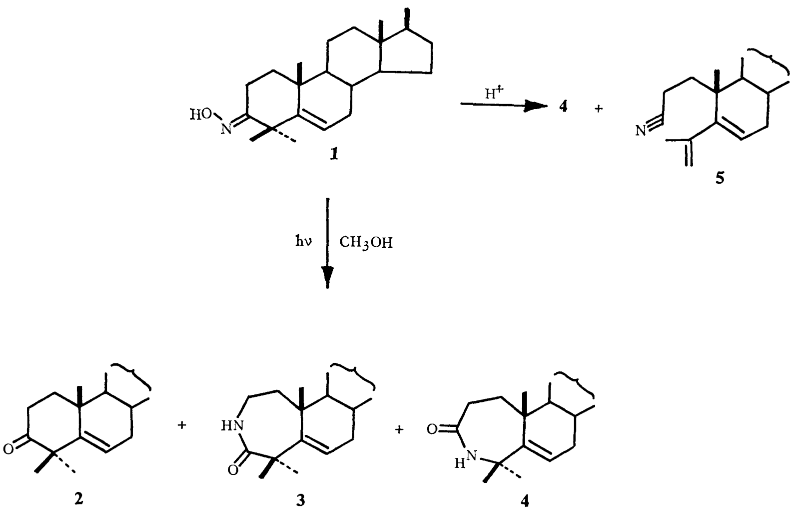
4,4-Dimethylcholest-5-en-3-one oxime (**1**) and 4,4,6-trimethylcholest-5-en-3-one oxime (**12**), prepared from the parent ketones (**2** and **11**)[8,9] by the standard method, were chosen as steroidal β,γ-unsaturated ketone oximes. 4,4,6-Trimethylcholest-5-en-3-one (**11**)[9] was prepared from 5,6α-epoxy-5α-cholestan-3β-ol (**6**) *via* 4 steps (Scheme 4).[10–12] In the course of these preparations, it was found that the reaction of epoxide (**6**) with methylmagnesium iodide to yield 6β-methyl-5α-cholestane-3β,5α-diol (**7**)[12] is accompanied by at least 6% yield of 3β-hydroxy-5α-cholestan-6-one (**8**)[12,13] resulting from a hydride shift followed by isomerization.

^{1}H NMR spectroscopy proved that the conformation of the ring A of oximes **1** and **12** is a *quasi* boat, as in the corresponding ketones,[14] and that the geometries of their hydroxyimino groups are *syn* with respect to their $C_{(2)}$–$C_{(3)}$ bond. Thus, the chemical shifts of the 19-H of the oximes **1** and **12** deviated considerably from those predicted by the additivity rule, indicating that their ring A is in a non-chair conformation; signals due to the 19-H of the oximes **1** and **12** were found at τ 9.14 and 9.19, whereas chemical shifts of their 19-H predicated by the additivity rule of deshielding effects[15] are about τ 8.79 based on the chemical shift (τ 9.10) of the 19-H of (*E*)- and (*Z*)-5α-cholestan-3-one oximes,[16] the ring A of which is in a chair conformation. Inspections of the Dreiding model indicated that when their ring A takes a *quasi* boat conformation, their hydroxyimino groups are almost eclipsed by their 2β-H. Thus, when the hydroxyl group is *syn* with respect to the $C_{(2)}$–$C_{(3)}$ bond, their 2β-H is deshielded.[2] The ^{1}H NMR spectrum of oximes **1** and **12** showed one-proton multiplets at τ 6.78—7.26 and at τ 6.79—7.19. These signals are assigned to their 2β-protons in the *quasi* boat conformations.[17] There were other one-proton double doublet centered at τ 7.59 (J=7.5 and 19.2 Hz) and at τ 7.68 (J=7.5 and 18.6 Hz) in the spectra of the oximes **1** and **12**. These signals are assigned to their 2α-proton on the basis of their chemical shifts and coupling constants.

A preliminary experiment showed that irradiation of oxime **1** in methanol until all the oxime was photolyzed would cause the secondary decompositions of appreciable amounts of product lactams. Therefore, irradiation was discontinued after three hours when TLC indicated that still about a half of the starting oxime remained unchanged. At this point, besides the starting oxime, spots due to the parent ketone (**2**) and two products were detected. Column chromatography afforded the parent ketone **2** (11%), the starting oxime **1** (53%), and two new products, **3** (10%) and **4** (9%) successively. The structures of

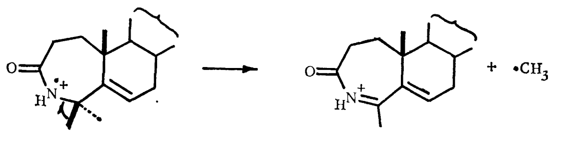
---

** Present address: Organic Chemistry Laboratory, Department of Chemical Process Engineering, Faculty of Engineering, Hokkaido University, Sapporo 060.



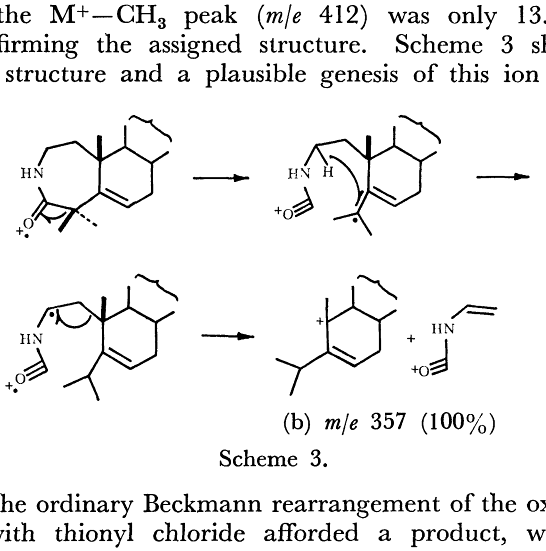
Scheme 1.

3 and **4** were determined to be 4a,4a-dimethyl-3-aza-*A*-homocholest-5-en-4-one (**3**) and 4a,4a-dimethyl-4-aza-*A*-homocholest-5-en-3-one (**4**) by their NMR, IR, and MS spectra (Scheme 1). The mass spectrum[18] of lactam **4** showed a weak molecular ion peak at *m*/*e* 427; the M^+-CH_3 fragment peak was the base peak assignable to an immonium species (a) in Scheme 2. In contrast, the mass spectrum of lactam **3** showed a distinct molecular ion peak at *m*/*e* 427 and the base peak at *m*/*e* 357. The intensity of the M^+-CH_3 peak (*m*/*e* 412) was only 13.5%, confirming the assigned structure. Scheme 3 shows the structure and a plausible genesis of this ion (b).



(a) *m*/*e* 402 (100%)

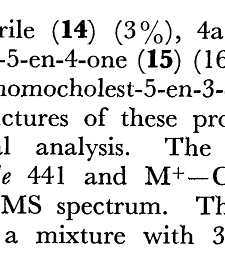
Scheme 2.



(b) *m*/*e* 357 (100%)

Scheme 3.

The ordinary Beckmann rearrangement of the oxime **1** with thionyl chloride afforded a product, which was shown to be a seconitrile (**5**) resulting from the second order Beckmann rearrangement by the MS, IR, and NMR (Table 1) spectra, and only a trace amount of the lactam **4** (Scheme 1). The mass spectrum of seconitrile **5** showed the molecular ion at *m*/*e* 409 as the base peak and only three distinct peaks at *m*/*e* 394 (M^+-CH_3), *m*/*e* 355, and *m*/*e* 296 ($M^+-C_{(17)}$ substituent) beyond *m*/*e* 200. The species *m*/*e* 355 is assignable to a species (c).



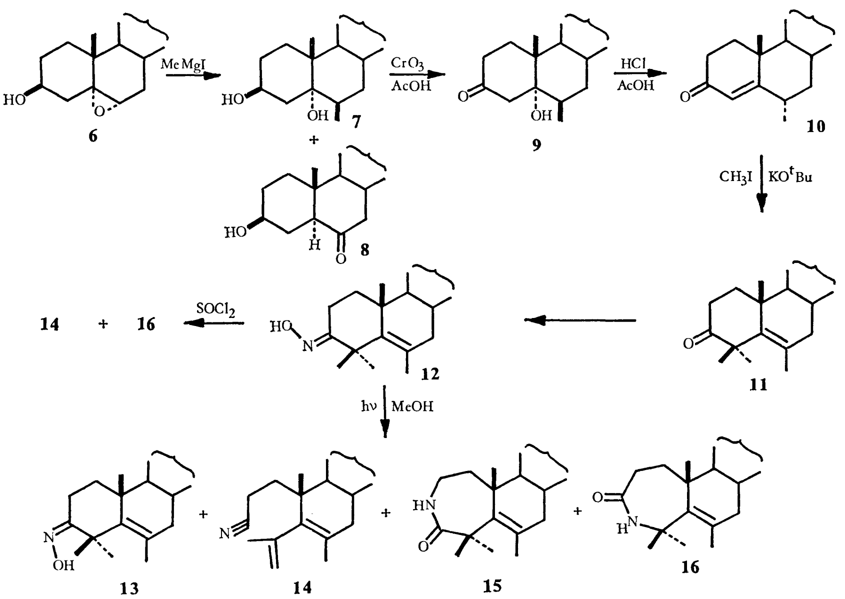
(c) *m*/*e* 355

Photoreaction of the oxime **12** in methanol was performed under conditions similar to those used for the photoreaction of the oxime **1**. Three-hour irradiation gave an isomeric oxime (**13**) (10%), the starting oxime **12** (41%), 4,6-dimethyl-4-methylene-3,4-seco-cholest-5-ene 3-nitrile (**14**) (3%), 4a,4a,6-trimethyl-3-aza-*A*-homocholest-5-en-4-one (**15**) (16%), and 4a,4a,6-trimethyl-4-aza-*A*-homocholest-5-en-3-one (**16**) (11%) (Scheme 4). Structures of these products were confirmed by spectral analysis. The isomeric oxime showed M^+ of *m*/*e* 441 and M^+-CH_3 peak as the base peak in the MS spectrum. The nitrile **14** was obtained only as a mixture with 3-aza lactam **15**; the yield was estimated by NMR spectroscopy. The $C_{(2)}$ methylene protons in the ^{1}H NMR spectrum of 3-aza lactam (**15**) appeared as two broad signals centered at τ 6.48 and 7.05. After D_2O exchange of the NH proton, the signal at τ 6.48 changed to a broad triplet and the signal at τ 7.05 to a broad doublet. Irradiation at τ 8.41 changed the broad triplet to a sharper triplet with J=13.5 Hz and the broad doublet to a double doublet (J=13.5 and 4.5 Hz). The splittings and the results of the decoupling experiments exclude a *quasi* chair conformation and are consistent with a *quasi* boat conformation of the ring A, in which the C_6–CH_3 bond nearly bisects the angle between gem dimethyl at $C_{(4a)}$; the dihedral angles between the 1β- and 2β-protons, the 1β- and 2α-protons, the 1α- and 2β-protons, and the 1α- and 2α-protons are around 40°, 160°, 80°, and 40°, respectively. Assuming this conformation and that the signal at τ 8.41 arises

Table 1. NMR parameters (100 MHz) for 5α-cholestane derivatives, 4,4-dimethylcholest-5-en-3-one 4,4,6-trimethylcholest-5-en-3-one, their oximes, and the reaction products in $CDCl_3$ solution [chemical shifts (τ) and splittings (Hz; in parenthesis)]

Compound	2-Methylene	6-H	18-H	19-H	4-Methyl	4-Methylene	NH	Others
1	a)	4.38(dd) (1.8 and 4.5)	9.29(s)	9.14(s)	8.63(s) and 8.70(s)	—	—	
2	a)	4.50(bs)	9.31(s)	9.15(s)	8.77(s)	—	—	
3	a)	4.10(dd) (1.5 and 4.5)	9.28(s)	8.70(s)	8.47(s) and 8.76(s)	—	4.16(bs)	
4	6.1—7.2(m)	4.12(dd) (1.8 and 6.3)	9.32(s)	8.91(s)	8.53(s) and 8.63(s)	—	3.72(bt) (6.7)	
5	a)	4.35(bd)	9.33(s)	8.86(s)	8.07(s)	5.17(bd)(15.0 and 1)	—	
7	a)	a)	9.31(s)	8.93(s)	—	a)	—	3α-H, 5.88(bs)
8	a)	—	9.37(s)	9.24(s)	—	—	—	3α-H, 6.45(bs)
9	a)	a)	9.30(s)	8.76(s)	—	—	—	4α-H, 7.02(d) J=13.5 4β-H, 7.99(d) J=13.5
10	a)	a)	9.31(s)	8.85(s)	—	4-H, 4.26(s)	—	6α-methyl, 8.96(d) J=6.0
11	a)	—	9.32(s)	9.25(s)	8.65(s) and 8.59(s)	—	—	6-methyl, 8.25(s)
12	2β-H, 6.79—7.19 (m), 2α-H, 7.68(dd) J=7.5 and 18.6 Hz	—	9.33(s)	9.19(s)	8.60(s) and 8.49(s)	—	—	6-methyl, 8.19(s)
13	a)	—	9.32(s)	8.91(s)	8.66(s) and 8.62	—	—	6-methyl, 8.23(s)
14	a)	—	9.32(s)	8.98(s)	8.15(s)	4.91(bs) $W_{1/2}$=6 Hz 5.47(bs) $W_{1/2}$=6 Hz	—	6-methyl, 8.15(s)
15	after D_2O exchange 6.48, 1H(bt) J=14 7.05, 1H(bd) J=15	—	9.35(s)	8.95(s)	two of 8.14, 8.26 and 8.56(each s)	—	4.12(t) J=6	6-methyl, one of 8.14, 8.26 and 8.56(each s)
16	a)	—	9.32(s)	8.76(s)	two of 8.14, 8.17 and 8.47(each s)	—	4.31(s)	6-methyl, one of 8.14, 8.17 and 8.47(each s)

a) Unassignable.



Scheme 4.

from the 1α-proton, the signals at τ 6.48 and 7.05 can be assigned to the 2α- and 2β-protons with $J_{2\alpha,2\beta}$ = 13.5 Hz, $J_{1\beta,2\alpha}$ = 13.5 Hz, and $J_{1\beta,2\beta}$ = 4.5 Hz respectively. Such assignments fit in with the coupling constants required by the above dihedral angles. Two 1,3-diaxial interactions of methyl groups are involved in the chair conformation of the 3-aza lactam. This interaction prohibits the lactam from taking the chair conformation. Fragmentations in the mass spectra of the nitrile **14** and the lactams **15** and **16** were entirely analogous to those of the nitrile **5** and the lactams **3** and **4**, respectively. Thus, the MS spectra of the lactams **15** and **16** showed their base peaks at *m/e* 371 and at *m/e* 426, corresponding to the species (b) and (a).

The ordinary Beckmann rearrangement of the oxime **12** was also studied. The treatment of oxime **1** with thionyl chloride gave two products, nitrile **14** and 4-aza lactam **15**, in 46 and 44% yields.

The present experiments confirmed that cyclic β,γ-unsaturated ketone oximes undergo photo-Beckmann rearrangements to lactams in yields comparable to those in the case of cyclic saturated ketone oximes.[2] Such results reinforce our previous conclusion[2,3] that the lactam formation resulting from the photo-rearrangement of cyclic saturated ketone oximes does not involve coupling of biradical or ions since, if a radical pair or ion pair were involved in the present photoreaction, these species would lead immediately to seconitriles; also, lactam formation by recombination of the cleaved species in the present case is very unlikely. Since there is a difference in the major products between acid-catalyzed reactions and photoreactions, the present photoreaction is of value for synthesis of unsaturated lactams (*e.g.*, **3** and **15**) which are not readily accessible by the ground state reactions.

Experimental

For instruments used and general procedures see Ref. 2. IR spectra were determined for Nujol mull with a JASCO IRA-1 spectrophotometer. The MS were recorded with a Hitachi JMS-D 300 spectrometer (direct inlet system, ion source temperature, *ca.* 180 °C, ionizing voltage, 70 eV) in the Faculty of Pharmaceutical Sciences or the Faculty of Agriculture. Only the Fragment peaks of the relative intensities over 20% for the lactams **3** and **4** and those over 30% for the seconitrile **5** are described.

Preparation of 4,4-Dimethylcholest-5-en-3-one Oxime (1). To a solution of 4,4-dimethylcholest-5-en-3-one (**2**) (800 mg) in methanol (200 ml) was added a solution of hydroxylamine hydrochloride (1 g) and sodium acetate trihydrate (1 g) in water (4 ml). The solution was stirred at 40 °C for 1.5 h and a further amount of methanol (100 ml) was added to the solution. The solution was refluxed for 2.5 h. The solvent was partly removed and the solution was extracted with diethyl ether. The diethyl ether solution was worked up in the usual way and evaporated. The residue was recrystallized from diethyl ether–methanol to afford the oxime **1** (726 mg), mp 223—226 °C. (Found: C, 81.26; H, 11.48; N, 3.14. Calcd for $C_{29}H_{49}NO$: C, 81.44; H, 11.55; N, 3.28%); IR 3304 (OH), 949 and 929 cm^{-1}; for NMR see Table 1; UV_{max} (MeOH) 207 nm (ε 5100).

The Photo-Beckmann Rearrangement of 4,4-Dimethylcholest-5-en-3-one Oxime (1). The oxime **1** (79 mg) in methanol (special grade, Wako) (230 ml) was irradiated with a Rayonet RPR-208 preparative photochemical reactor under an atmosphere of nitrogen for 3 h. TLC indicated four spots, due to the parent ketone **2**, the unchanged oxime **1**, and two lactams, in the order of their mobility. Three further photoreactions (80, 81, and 66 mg) were carried out under the same procedure. Products from the four photolyses were combined and subjected to column chromatography (Wako gel C-200, 10 g). Elution with a 3:1 mixture of benzene and hexane gave the parent ketone (32 mg). Further elutions with a 19:1 mixture of benzene and hexane and with pure benzene gave oxime **1** (162 mg). Successive elutions with a 4:1 mixture of benzene and ethyl acetate gave 3-aza lactam **3** (30 mg) which was recrystallized from methanol. Mp 175—177 °C. (Found: C, 81.30; H, 11.32; N, 3.10%. Calcd for $C_{29}H_{49}NO$: C, 81.44; H, 11.55; N, 3.28%); $[\alpha]_D^{18}$ −4.2° (*c* 0.5 $CHCl_3$); IR 1657 (lactam carbonyl), 3062 and 3198 cm^{-1} (NH); for NMR see Table 1;

MS *m/e* (rel intensity) 429 (M^+, 1.9), 427 (30.8), 358 (29.5), 357 (100), and 42 (24.2). Continued elutions with the same solvent mixture gave 4-aza lactam **4** (29 mg), which was recrystallized from methanol. Mp 198.5—201.0 °C. (Found: C, 80.86; H, 11.69; N, 3.21%. Calcd for $C_{29}H_{49}NO$: C, 81.44; H, 11.55; N, 3.28%); $[\alpha]^{20}_D$ −11.3° (*c* 1.0 $CHCl_3$); IR 1656 and 1611 (lactam carbonyl) 3062 and 3198 cm^{-1} (NH); for NMR see Table 1; MS *m/e* (rel intensity) 42 (M^+ 0.4), 427 (3.7), 413 (31.5), 412 (100), and 58 (26.6).

*The Beckmann Rearrangement of 4,4-Dimethylcholest-5-en-3-one Oxime (**1**).* To a solution of the oxime **1** (200 mg) in dioxan (10 ml) was added some freshly purified thionyl chloride (0.1 ml) at room temperature. The solution was stirred for 20 min at room temperature and poured into water. The mixture was neutralized with sodium hydrogencarbonate. The aqueous solution was extracted with diethyl ether. The diethyl ether solution was worked up as usual. TLC showed that the product (184 mg) (R_f= 0.8) is nearly a single compound, with only traces of minor products (R_f=0.1 and 0). The residue was subjected to preparative TLC with benzene. The more mobile major product (162 mg) was recrystallized from methanol to afford the nitrile (**8**), mp 43.5—45.0 °C, (54 mg). (Found: C, 84.68; H, 11.39; N, 3.41. Calcd for $C_{29}H_{47}N$: C, 85.02; H, 11.56; N, 3.42%); IR 2243 (C≡N), 1610 and 906 cm^{-1}; for NMR see Table 1; MS *m/e* (rel intensity) 409 (100, M^+), 394 (28.7), 296 (33.6), 147 (30.9), 145 (52.3), 121 (31.1), 107 (32.6), 105 (40.2), 95 (46.9), 93 (34.0), 81 (47.1), 69 (41.4), 57 (53.6), 55 (66.2), 43 (70.4), and 41 (55.3). The less mobile fraction (10 mg) was an unidentified gum. The least mobile fraction (R_f=0) (19 mg) was recrystallized from methanol to afford 4-aza lactam **4**, identical with the specimen obtained by the photo-Beckmann rearrangement.

*Reaction of 5,6α-Epoxy-5α-cholestan-3β-ol (**6**) with Methylmagnesium Iodide.*[11,12] A solution of epoxide **6** (18.8 g) in dry benzene (300 ml) was added to a solution of methylmagnesium iodide prepared with magnesium (4.6 g) and methyl iodide (30 ml) in dry diethyl ether (50 ml) and dry benzene (100 ml). The solution was refluxed for 5 h. After cooling, aqueous solution of ammonium chloride (300 ml) was added and the solution was extracted with diethyl ether (200 ml). After the usual work-up, the product was recrystallized from diethyl ether–ethanol to give 6β-methyl-5α-cholestane-3β,5α-diol **7** (3.3 g). The residue from the filtrate was subjected to column chromatography. (alumina, 660 g). Elutions with a 1:1 mixture of hexane and benzene and then benzene gave a fraction (2.78 g) which was recrystallized from methanol to give 3β-hydroxy-5α-cholestan-6-one (**8**) (1.12 g, 6%) mp 148—150 °C (lit,[11] 145—146 °C). The acetate, mp 129—131.5 °C (methanol) (lit,[12] 128—129 °C), was obtained in usual way. Continued elutions with benzene gave a second fraction which was recrystallized from dichloromethane–ethanol to give an additional 3β,5α-diol **7** (5.59 g), 182—183 °C (lit,[11] 182—183 °C). The total yield of the diol was 47%.

*Preparation of 6α-Methylcholest-4-en-3-one (**10**).*[9] Diol **7** (13 g) in acetic acid (240 ml) was oxidized with chromium trioxide.[10] The crude 5α-hydroxy-6β-methylcholestan-3-one (**9**) obtained was dissolved in acetic acid (100 ml). To this solution was added concd hydrochloric acid (10 mg). The solution was stirred for 13 h and was extracted with diethyl ether. The usual work-up afforded a residue which was subjected to column chromatography (Wako C-200, 400 g). Successive elutions with 1:3, 1:5, and 1:10 mixtures of hexane and benzene, benzene only, and a 1:10 mixture of benzene and diethyl ether gave a fraction which was once recrystallized from methanol to yield ketone **10**, mp 126—127 °C (lit,[9] 127—128.5 °C). For NMR spectrum see Table 1.

*Preparation of 4,4,6-Trimethylcholest-5-en-3-one (**11**).* The ketone **10** (360 mg) in dry *t*-butyl alcohol (6 ml) was added to potassium (110 mg) in the same solvent (100 ml) under a nitrogen atmosphere. Methyl iodide (0.33 ml) was added and the mixture was heated under reflux for 75 min. After the addition of methyl iodide (0.1 ml) the solution was heated under reflux for an additional 25 min. The solution was extracted with dichloromethane and the organic layer was worked up in the usual manner. The product was subjected to preparative TLC with benzene to yield ketone **11** (189 mg). Recrystallization from methanol gave the pure material, mp 134—136 °C. (Found: C, 84.39; H, 11.84%. Calcd for $C_{30}H_{50}O$: C, 84.44; H, 11.81%); $[\alpha]^{21}_D$=−7.8° (*c* 1.1 $CHCl_3$); IR 1609 (carbonyl), and 1026 cm^{-1}.

*Preparation of 4,4,6-Trimethylcholest-5-en-3-one Oxime (**12**).* The ketone **11** (770 mg), hydroxylamine hydrochloride (2.5 g), and sodium acetate trihydrate (2.5 g) in a mixture of ethanol (300 ml) and water (15 ml) were refluxed for 2 d. After the addition of a further amount of hydroxylamine hydrochloride (1 g) in water (3 ml), the solution was refluxed for another 3 d. A part of the solvent was evaporated under a reduced pressure and the solution was extracted with diethyl ether. The ethereal solution was worked up in the usual way and the product was subjected to column chromatography (silica gel Wako C-200, 27 g). Elutions with a 1:3 mixture of hexane and benzene gave the starting material (384 mg after recrystallization from methanol) and continued elutions gave the oxime **12**. The oxime was recrystallized from aq methanol to yield crystals (339 mg, 43%), mp 179.0—180.5 °C. (Found: C, 81.17; H, 11.89; N, 3.33%. Calcd for $C_{30}H_{51}NO$: C, 81.57; H, 11.64; N, 3.17%); $[\alpha]^{21}_D$ −3.2 (*c* 1.0 $CHCl_3$); IR 3311 (OH), 949, 918, and 720 cm^{-1}; MS *m/e* (rel intensity), 441 (M^+, 32.9), 426 (M^+-CH_3, 82.7), 425 (M^+-O, 29.8), 424 (M^+-OH, 100), 369 (25.0), 95 (32.8), 57 (26.7), 55 (29.6), and 43 (33.3). For the NMR see Table 1. UV_{max}(MeOH) 208 nm (ε 7600).

*The Photo-Beckmann Rearrangement of 4,4,6-Trimethylcholest-5-en-3-one Oxime (**12**).* Oxime **12** (80 mg) in methanol (special grade, Wako) (230 ml) was irradiated with a preparative photochemical reactor under an atmosphere of nitrogen for 4 h. TLC indicated five spots due to an isomeric oxime (**13**), a recovered oxime **12**, nitrile **14**, and two lactams **15** and **16**, in the order of their mobility. The photoreaction was repeated three times under the same conditions as the first one (80, 81, and 81 mg) and the products were combined and subjected to column chromatography. Elutions with a 3:1 mixture of benzene and hexane gave four fractions: A (32 mg), B (146 mg), C (61 mg), and D (35 mg). Fraction A was isomeric oxime **13** and was recrystallized from methanol. Mp 145—148 °C. IR, 3450 cm^{-1} (OH); MS *m/e* (rel intensity) 441 (M^+, 14.0), 426 (M^+-CH_3, 100), 424 (M^+-OH), 411 (51.4), 410 (51.0), 369 (77.2), 327 (26.9), 95 (83.7), 57 (74.2), 55 (79.2), and 43 (96.5). For NMR spectra see Table 1. Fraction B was recovered oxime **12**. Fraction C was a mixture of seconitrile **14** and 3-aza lactam **15**, based on its NMR analysis. Its recrystallization from methanol gave pure 3-aza lactam **15** (42 mg), mp 197—199 °C. (Found: M^+, *m/e* 441.3969). Calcd for $C_{30}H_{51}NO$: M^+ 441.3969; $[\alpha]^{21}_D$ −33.6 (*c* 0.25 $CHCl_3$); IR 3250 (NH), 1677 and 1742 (lactam carbonyl), and 720 cm^{-1}; MS *m/e* (rel intensity) 441 (M^+, 0.4), 426 (M^+-CH_3, 2.1), 398 (1.0), 372 (20.0), and 371 (100); for NMR see Table 1.

The residue (19 mg) from the filtrate in the above recrystallization was a 1:1 mixture of nitrile **14** and 3-aza lactam **15**, as estimated by the relative intensities of the signals due to their 10β-methyl in the NMR spectrum. Fraction D was 4-aza lactam **16**, which was recrystallized from methanol. Mp 178—180 °C. (Found: C, 81.33; H, 11.72; N, 3.14%. Calcd for $C_{30}H_{51}NO$: C, 81.57; H, 11.64; N, 3.17%); $[\alpha]^{22}_{D}$ -31.7 (*c* 1.0 $CHCl_3$); IR 3240 (NH), 1685 (lactam carbonyl), and 774 cm^{-1}; MS *m/e* (rel intensity) 441 (M^+, 3.4), 426 (M^+-CH_3, 100), and 58 (55.0); for the NMR see Table 1.

The Beckmann Rearrangement of 4,4,6-Trimethylcholest-5-en-3-one Oxime. To oxime **12** (74 mg) in dry dioxane (3 ml) and dry diethyl ether (0.1 ml) was added thionyl chloride (0.5 ml) at 0 °C. The solution was stirred for 30 min at 10 °C. The solution was extracted with diethyl ether and the organic layer was washed with 5% sodium hydrogencarbonate and water successively and dried. The product was subjected to preparative TLC with benzene to give three major fractions: A (34 mg), B (10 mg), and C (33 mg), in the order of their mobility. Fraction A was an oil and was identified as seconitrile **14**. (Found: N, 3.34%. Calcd for $C_{30}H_{49}N$: N, 3.31%); MS *m/e* (rel intensity), 423 (M^+, 26.7), 408 (M^+-CH_3, 20.2), 369 ($M^+-C_{(10)}$ side chain, 100), 265 (9.8), and 57 (54.9); for NMR see Table 1. Fraction C was 4-aza lactam **16**, which was recrystallized from methanol to afford a pure specimen (18 mg). It was identical with **16** obtained by the photoreaction.

We thank Mrs. T. Okayama and Miss H. Maki for ^1H NMR measurements and spin decoupling experiments.

References

1) Photoinduced Transformations. Part 56. Part 55. H. Suginome, H. Ono, and T. Masamune, *Bull. Chem. Soc., Jpn.*, **54**, 852 (1981).

2) H. Suginome and H. Takahashi, *Bull. Chem. Soc. Jpn.*, **48**, 576 (1975); H. Suginome and F. Yagihashi, *J. Chem. Soc., Perkin Trans. 1*, **1977**, 2488.

3) For a review of the Photo-Beckmann Rearrangement, see H. Suginome, *Kagaku No Ryoiki*, **30**, 578 (1976).

4) H. Suginome and Chi-Ming Shea, *Synthesis*, **1980**, 229.

5) H. Suginome and Chi-Ming Shea, *J. Chem. Soc., Perkin Trans. 1*, **1980**, 2268.

6) H. Suginome and T. Uchida, *Bull. Chem. Soc., Jpn.*, **47**, 687 (1974); H. Suginome and T. Uchida, *Bull. Chem. Soc. Jpn.*, **53**, 2292 (1980).

7) L. S. Kaminsky and M. Lamchen, *J. Chem. Soc., C*, **1966**, 2295; J. Parello, M. Riviere, E. Desherces, and A. Lattes, *C. R. Acad. Sci.*, **273**, 1097 (1971); E. Desherces, M. Riviere, J. Parello, and A. Lattes, *ibid.*, Ser. C, **275**, 581 (1972); D. St. C. Black and K. G. Watson, *Aust. J. Chem.*, **26**, 2505 (1973); D. St. C. Black, N. A. Blackman, and A. B. Boscacci, *ibid.*, **32**, 1775 (1979).

8) R. B. Woodward, A. A. Patchett, D. H. R. Barton, D. A. J. Ives, and R. B. Kelly, *J. Chem. Soc.*, **1957**, 1131.

9) R. J. Abraham and J. S. E. Holker, *J. Chem. Soc.*, **1963**, 806.

10) R. B. Turner, *J. Am. Chem. Soc.*, **74**, 5362 (1952).

11) M. I. Ushakov and O. S. Madaeva, *J. Gen. Chem. (USSR)*, **9**, 436 (1939).

12) L. F. Fieser and J. Rigaudy, *J. Am. Chem. Soc.*, **73**, 4660 (1951).

13) I. M. Heilbron, H. Jackson, E. R. H. Jones, and F. S. Spring, *J. Chem. Soc.*, **1938**, 102.

14) a) M. Gorodetsky and Y. Mazur, *Tetrahedron Lett.*, **1966**, 227; M. Gorodetsky, A. Yogev, and Y. Mazur, *J. Am. Chem. Soc.*, **31**, 699 (1966); b) B. B. Dewhurst, J. S. E. Holker, A. Lablache-Combier, M. R. G. Leeming, J. Levisalles, and J. P. Pete, *Bull. Soc. Chim. Fr.*, **1964**, 3259; c) G. Ferguson, W. C. Marsh, J. M. Midgley, and W. B. Whalley, *J. Chem. Soc., Perkin Trans. 2*, **1978**, 272; d) U. Burkert and N. L. Allinger, *Tetrahedron*, **34**, 807 (1978).

15) J. N. Shoolery and M. T. Rogers, *J. Am. Chem. Soc.*, **80**, 5121 (1958); R. F. Zürcher, *Helv. Chim. Acta*, **44**, 1380 (1961).

16) C. W. Shoppee, G. Krüger, and R. N. Mirrington, *J. Chem. Soc.*, **1962**, 1050.

17) The conclusions on the conformations of the ring A and the geometries of hydroxyimino groups of oximes **1** and **12** are further supported by a study of the ^1H NMR spectrum of 17β-acetoxy-4,4-dimethyl-19-norandrost-5-en-3-one oxime prepared by A. Osada in this laboratory. The ring A of this oxime should be in a *quasi* chair conformation since no 1,3-diaxial interaction of methyl groups is involved in the molecule. In fact, its NMR spectrum showed a one-proton double doublet at τ 6.74 with $J=13.5$ and 4.5 Hz. The chemical shift and the coupling constants are in agreement with those of the 2α-proton deshielded by the adjacent hydroxyimino group in the ring A in a *quasi* chair conformation.

18) a) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco (1967), p. 353; b) H. Budzikiewicz, F. Compernolle, K. V. Cauenberghe, K. Schulze, H. Wolf, and G. Quinkert, *Tetrahedron*, **24**, 6797 (1968).