J. Serb. Chem. Soc. 69 (6) 413–420 (2004)
JSCS – 3168

UDC 66.095.213+541.143:547.288.4
Original scientific paper

Photochemical and Beckmann rearrangement of (*Z*)-cholest-4-en-6-one oxime

NATALIJA M. KRSTIĆ[a*#], MIRA S. BJELAKOVIĆ[a#], MILAN M. DABOVIĆ[a#], LJUBINKA B. LORENC[a,b#] and VLADIMIR D. PAVLOVIĆ[b,a#]

[a]*Center for Chemistry, ICTM, P. O. Box 473, 11001 Belgrade and* [b]*Faculty of Chemistry, University of Belgrade, Studentski trg 12–16, P. O. Box 158, 11001 Belgrade, Serbia and Montenegro*
(e-mail: nkrstic@chem.bg.ac.yu)

(Received 27 November 2003)

Abstract: Beckmann rearrangement of (*Z*)-cholest-4-en-6-one oxime (**4**) (prepared in 4 steps starting from cholest-5-en-3β-ol (**1**)) with thionyl chloride in dioxane solution afforded an enamide-type lactam, *i.e.*, 7-aza-B-homocholest-4-en-6-one (**6**) as a single product. Photoreaction of the same compound in methanol or benzene-acetic acid solution gave a mixture of products, with the formation of the parent ketone **3** and the occurrence of *Z*/*E* isomerization, while the lactam **6** was obtained only when the reaction was performed in methanol and then in very low yield (7 %).

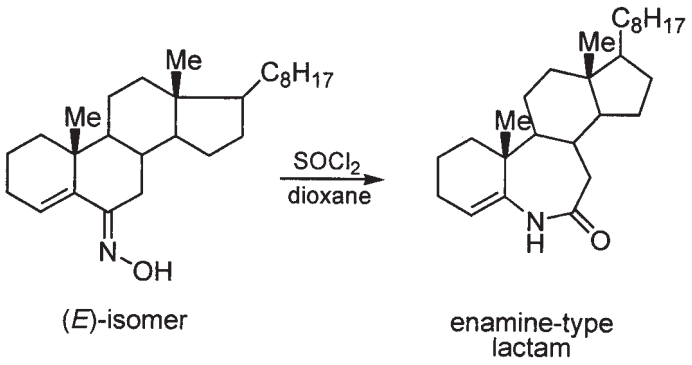
Keywords: (*Z*)-cholest-4-en-6-one oxime, 7-aza-B-homocholest-4-en-6-one, Beckmann rearrangement, photoreaction.

INTRODUCTION

It is well known that ground-state Beckmann rearrangements of steroidal α,β-unsaturated ketone oximes in the *E*-configuration usually lead to the formation of enamine-type lactams, as depicted in Scheme 1.

However, under protic photolytic conditions, in methanol or benzene-acetic acid solution, steroidal α,β-unsaturated ketone oximes, depending on their structural features, can react in two ways. Thus, excited oximes having their C=C bond at the non-ring junction principally undergo photoisomerization to form a transient corresponding to their geometrical isomers, from which stereospecific additions of protons or methanol to their C=C bond takes place, while oximes having their C=C bond at the ring junction undergo photorearrangement to give the corresponding enamides.[1] Most of these photolytic reactions were performed using (*E*)-isomers or a mixture of (*Z*)-

* Corresponding author
\# Serbian Chemical Society active member



Scheme 1.

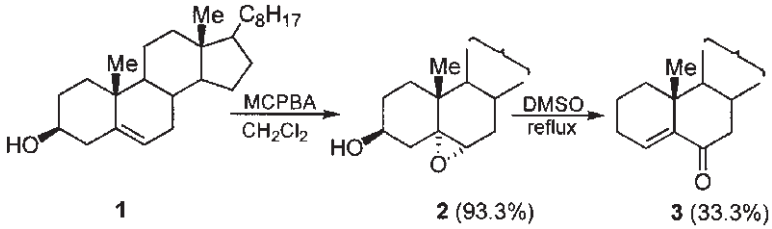
and (*E*)-isomers, such as (*Z*)- and (*E*)-cholest-4-en-3-one oximes.[2] In the course of work directed towards the synthesis of 6-aza-steroid derivatives as biologically active molecules, it was considered to be of interest to investigate the behaviour of pure (*Z*)-stereoisomeric oximes, *e.g.*, (*Z*)-cholest-4-en-6-one oxime (**4**), under similar photolytic and thermal conditions.

RESULTS AND DISCUSSION

Synthesis of (Z)-*cholest-4-en-6-one oxime (4)*

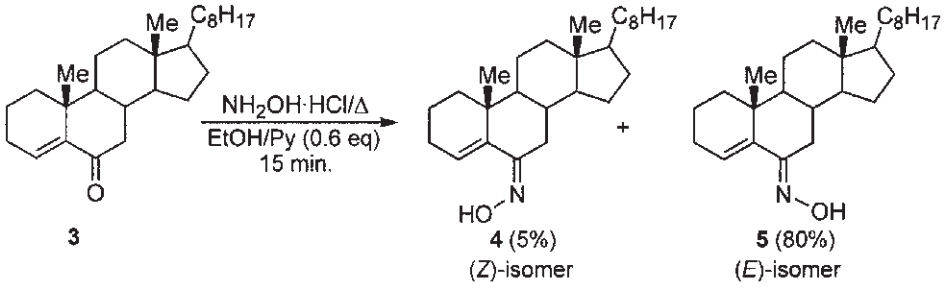
The key intermediate in the synthesis of oxime **4** is cholest-4-en-6-one (**3**). There are several methods for the preparation of this compound all starting from 5,6α-epoxy-5α-cholesterol[1] or its 3α-chloro- or 3β-acetoxy-derivatives.[3]

It was found that this enone can be most conveniently prepared according to the procedure reported by Miljković *et al.*[4] in which 3β-hydroxy-5,6α-epoxy-5α-cholestane (**2**) (obtained by epoxidation of cholesterol) is refluxed in dimethyl sulfoxide solution. In this very simple way, the required cholest-4-en-6-one (**3**) was obtained in 33.3 % yield (Scheme 2).



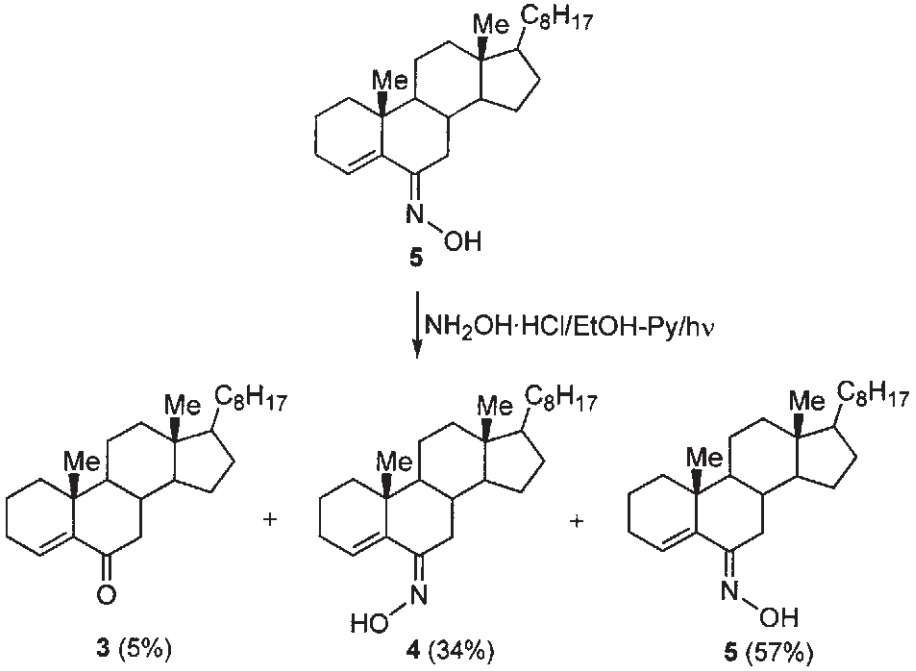
Scheme 2.

Oximation of the enone **3** was carried out with hydroxylamine hydrochloride in refluxing ethanol-pyridine solution (9:1, v/v) for 15 min. After column chromatography of the reaction mixture on silica gel, the two stereoisomeric oximes, *i.e.* (*Z*)- and (*E*)-cholest-4-en-6-one oximes (**4**) and (**5**) were obtained in 5 %, and 80 % yields, respectively (Scheme 3).



Scheme 3.

The structure of these oximes was determined on the basis of their analytical and spectral data (IR, ^{1}H-NMR, ^{13}C-NMR, MS). IR spectra bands at 3312 and 3250 cm^{-1} for the (*Z*)- and (*E*)-isomer **4** and **5**, respectively, indicate the presence of a hydroxyimino group in both compounds. In the ^{1}H-NMR spectrum of compound **5**, the signal for H_{β}-C(7) (due to the deshielding influence of the hydroxy oxygen of the oxime, estimated to be 2.4 Å from H_{β}-C(7)), was shifted downfield, appearing at 3.29 ppm as a *doublet of doublets*, confirming the (*E*)-configuration. The signal for the corresponding proton in the (*Z*)-isomer **4** appeared at 2.39 ppm as a *fine doublet* (H_{β}-C(7)-O distance is about 3.8 Å). On the other hand, the high field position of the signal for the olefinic proton at C(4) (5.86 ppm in (*E*)-isomer **5** and 6.02 ppm in (*Z*)-isomer **4**) indicates that it is less deshielded by the hydroxyimino group than the parent 6-oxo group (6.38 ppm) in both isomers.



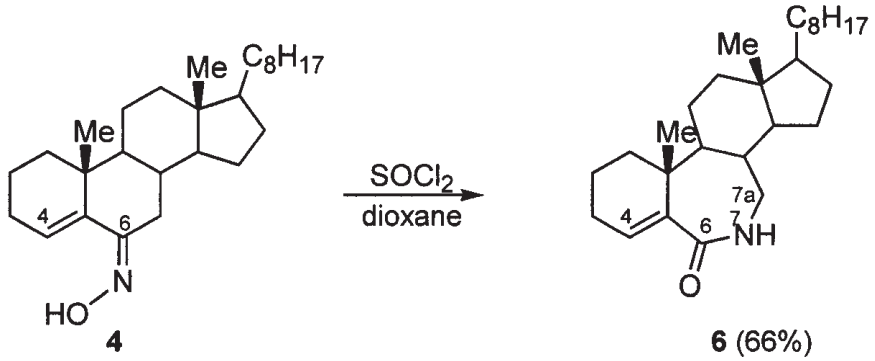
Scheme 4.

As shown in Scheme 3, the direct oximation of enone **3** gives the (*Z*)-isomer **4** as the minor product (formed in only *ca*. 5 % yield). A large amount of this (*Z*)-derivative **4** was obtained from the oxime **5** by *E*→*Z* isomerization.

Irradiation of (*E*)-cholest-4-en-6-one oxime (**5**) in ethanol/pyridine solution (9:1, v/v) was carried out using a high-pressure mercury lamp (TQ 150 Z2, Hanau), in the presence of $NH_2OH{\cdot}HCl$ (Scheme 4). This photoreaction, after column chromatography on SiO_2, gave the parent Δ^4-cholesten-6-one **3** (5 %), as well as the isomeric (*Z*)-oxime **4** in 34 % yield, and unchanged (*E*)-oxime **5** in 57 % yield.

Beckmann rearrangement of (Z)*-cholest-4-en-6-one oxime (4)*

Treatment of (*Z*)-cholest-4-en-6-one oxime (**4**) with thionyl chloride in dioxane solution gave as a single product an enamide-type lactam, *i.e.* 7-aza-B-homocholest-4-en-6-one (**6**) in 66 % yield (Scheme 5).



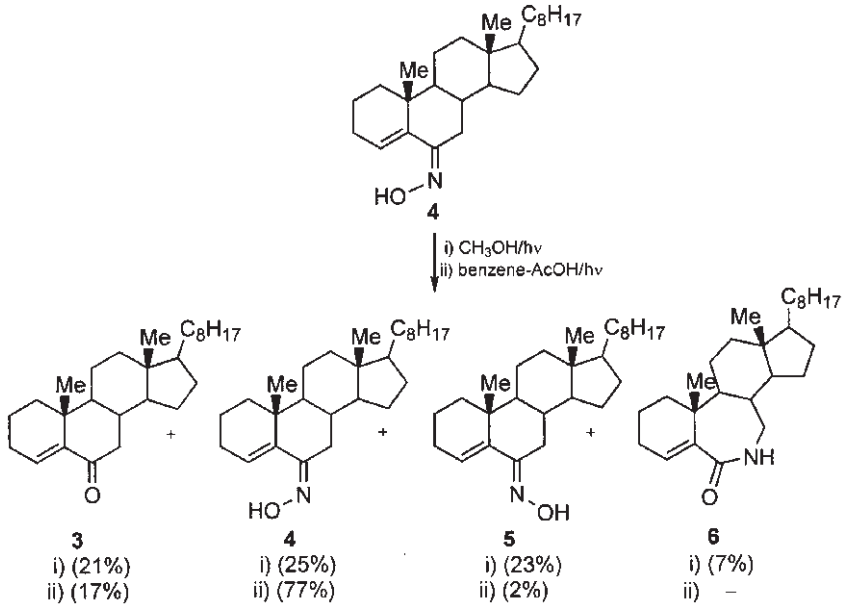
4 **6** (66%)

Scheme 5.

The structure of this compound was deduced from its analytical and spectral data. In ^{1}H-NMR spectrum, the signal for the olefinic proton H-C(4) (due to deshielding influence by the C(6)=O group) shifted downifield, appearing at 6.01 ppm. The same proton in the enamine-type lactam appears at 5.54 ppm. The signals atributable to methylene protons adjacent to an amide nitrogen, H_α-C(7a) and H_β-C(7a) appeared at 2.84 and 3.04 ppm, respectively, both as *ddd*. Also the signal for the amide proton at 6.43 ppm is situated upfield when compared to the signal for the same proton in the enamine lactam (8.01 ppm).

Photolysis of (Z)*-cholest-4-en-6-one oxime (4)*

The photoreaction of (*Z*)-cholest-4-en-6-one oxime (**4**) was carried out under argon using a 6 W low pressure mercury lamp (Applied Photophysics Ltd. G4T5) in i) methanol and ii) benzene-acetic acid (94:6) solutions. After 6 h irradiation of **4** in methanol a mixture of products containing the parent cholest-4-en-6-one (**3**) (21 %), unchanged oxime **4** (25 %), isomeric (*E*)-oxime **5** (23 %), and lactam **6** (7 %) (Scheme 6) was obtained. No lactam **6** was obtained even after 12 h irradiation of the oxime **4** in benzene containing glacial acetic acid. The only obtained product, besides the starting



Scheme 6.

oxime **4** (77 %) and a very small amount of *E*-isomer **5** (2 %), was the parent ketone **3** (17 %).

DISCUSSION

The foregoing results show that the thermal Beckmann rearrangement of (*Z*)-cholest-4-en-6-one oxime (**4**) gave the enamide-type lactam **6** (derived by migration of the 7-alkyl substituent) as a single product in very good yield (66 %). The results confirm that the initial geometry of the hydroxyimino group has a decisive influence on the direction of migration of the trigonal carbon to the nitrogen.

The photorearrangement of excited α,β-unsaturated (*Z*)-cholest-4-en-6-one oxime (**4**) in methanol takes place mostly due to *Z*/*E*-isomerization to the more stable (*E*)-isomer **5**, which then forms the cyclic enamide **6**, although only in a very low yield (7 %). This formation probably proceeds *via* the reorganization of the excited singlet oxaziridine formed from the excited singlet oxime.

Irradition of **4** in benzene with a small amount of glacial acetic acid resulted in no *Z*/*E* isomerization (only 2 % of the *E*-isomer was obtained) as well as rearrangement to lactam.

Suginome and his coworkers previously reported that, regardless of the configuration of the hydroxyimino group, only cyclic enone-type lactams can be obtained in the Beckmann rearrangement of steroidal cyclic α,β-unsaturated ketone oximes, which was explained by the phenomenon that *Z*/*E* isomerization occurs prior to C→N migration.[2] Under analogous experimental conditions, (*E*)-isomers of cholest-4-en-6-one oxime (**5**) and cholest-5-en-4-one oxime gave enamine-type lactams.[1]

EXPERIMENTAL

General

Removal of solvents was carried out under reduced pressure. Prep. column chromatography: silica gel Merck 0.063–0.200 mm and 0.040–0.063 mm. TLC: control of reaction and separation of products on silica gel 60 F_{254} (Merck) with benzene/EtOAc 9:1, 8:2 and 7:3, and with dichloromethane/methanol 19:1, detection with 50 % aq. H_2SO_2 soln. and with I_2. M.pts. uncorrected. IR spectra: Perkin-Elmer-337 spectrophotometer: ν in cm^{-1}. NMR spectra: Varian Gemini 200 (^{1}H at 200 MHz, ^{13}C at 50 MHz); $CDCl_3$ soln. at r.t., TMS as internal standard; chemical shifts in ppm as δ values, J in Hz. Mass spectra: Finnigan-MAT 8230.

*5,6α-Epoxy-5α-cholestan-3β-ol (**2**)*

A solution of cholesterol (**1**) (5.00 g) in CH_2Cl_2 (100 ml) was treated with 70 % *m*-chloroperbenzoic acid (MCPBA, 3.50 g) with stirring at room temperature for 2 h. After the usual work-up, the obtained residue (5.18 g, 99.4 %) was crystallized from acetone to give 5,6α-epoxy-5α-cholestan-3β-ol (**2**) (4.86 g, 93.3 %), m.p. 142–143 ºC, lit.[6] m.p. 142–144 °C. IR(KBr): 3400, 2938, 1466, 1043, 910. ^{1}H-NMR: 0.61 (*s*, 3H, CH_3(18)), 0.86 (*d*, 6H, CH_3(26), CH_3(27)), 0.89 (*d*, 3H, CH_3(21)), 1.05 (*s*, 3H, CH_3(19)), 2.89 (*d*, J = 3.4, H– C(6)), 3.01 (*br s*, 1H, HO–C(3)), 3.90 (*septet*, 1H, H–C(3)). ^{13}C-NMR: 68.2 (*d*, C(3)), 65.9 (*s*, C(5)), 59.3 (*d*, C(6)), 56.7 (*d*, C(17)), 55.7 (*d*, C(14)), 42.4 (*d*, C(9)), 42.1 (*s*, C(13)), 39.6 (*t*, C(4)), 39.3 (2*t*, C(12), C(24)), 36.0 (*t*, C(22)), 35.6 (*d*, C(8)), 34.7 (*s*, C(10)), 32.3 (*t*, C(7)), 30.7 (*t*, C(1)), 29.7 (*d*, C(20)), 28.6 (*t*, C(16)), 27.9 (*t*, C(15)), 27.8 (*d*, C(25)), 23.9 (*t*, C(2)), 23.7 (*t*, C(23)), 22.7 (*q*, C(27)), 22.4 (*q*, C(26)), 20.5 (*t*, C(11)), 18.5 (*q*, C(21)), 15.8 (*q*, C(19)), 11.7 (*q*, C(18)).

*Cholest-4-en-6-one (**3**)*

A solution of epoxide **2** (1.00 g) in DMSO (25 ml) was refluxed with stirring at 200–209 ºC until the starting compound had been consumed (about 1 h). The reaction mixture was then worked up with ether, washed with water, 5 % $NaHCO_3$ and water again, dried over $CaSO_4$ and evaporated to dryness to give an oily residue (0.82 g) which was chromatographed on SiO_2 (20g). Elution with *n*-hexane–toluene(9:1, 8:2, 7:3) afforded a complex mixture (0.23 g, 23 %) which was not further investigated. The white solid obtained by elution with *n*-hexane–toluene (6:4) was recrystallized from acetone to give cholest-4-en-6-one (**3**) (0.33 g, 33 %), m.p. 109–110 ºC. lit.[7] m.p. 107–108 ºC. IR (KBr): 1687, 1623. ^{1}H-NMR: 0.70 (*s*, 3H, CH_3(18)), 0.86 (*d*, 6H, CH_3(26), CH_3(27)), 0.92 (*d*, 3H, CH_3(21)), 0.97 (*s*, 3H, CH_3(19)), 6.38 (*t*, J = 3.2, 1H, H–C(4)). ^{13}C-NMR: 202.9 (*s*, C(6)), 145.7 (*s*, C(5)), 132.2 (*d*, C(4)), 56.6 (*d*, C(17)), 55.8 (d, C(14)), 50.8 (*d*, C(9)), 45.8 (*t*, C(7)), 42.3 (*s*, C(13)), 39.2 (2*t*, C(12), C(24)), 37.5 (*s*, C(10)), 35.9 (*t*, C(1)), 35.5 (*d*, C(20)), 35.3 (*t*, C(22)), 23.7 (*t*, C(23)), 23.6 (*t*, C(3)), 22.6 (*q*, C(27)), 22.4 (*q*, C(26)), 21.1 (*t*, C(11)), 20.4 (*q*, C(19)), 18.4 (*q*, C(21)), 17.7 (*t*, C(2)), 11.7 (*q*, C(18)).

(E)-*Cholest-4-en-6-one oxime (**4**)*

To a solution of cholest-4-en-6-one (**3**) (1.00 g) and hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$), (1.00 g) in EtOH, pyridine (6.6 mol) was added and the reaction mixture refluxed for 15 min. After evaporation of the solvent, the residue was dissolved in Et_2O, washed with water, dried over $CaSO_4$ and evaporated to dryness. The resulting mixture was chromatographed on SiO_2 (0.040–0.063 mm, 50 g). Elution with toluene–EtOAc (97:3) gave (*Z*)-cholest-4-en-6-one oxime (**4**) (0.052 g, 4.9 %), m.p. 153–157 ºC. IR (KBr): 3312, 2973, 1465, 968, 934. ^{1}H-NMR: 0.66 (*s*, 3H, CH_3(18)), 0.86 (*d*, 6H, CH_3(26), CH_3(27)), 0.90 (*d*, 3H, CH_3(21)), 0.96 (*s*, 3H, CH_3(19)), 2.39 (*fd*, J = 2.6, 12.4, 1H, H_β–C(7)), 6.02 (*dd*, J = 2.2, 5.1, 1H, H–C(4)), 9.36 (*br s*, 1H, =NOH). ^{13}C-NMR: 156.8 (*s*, C(6)), 136.2 (*s*, C(5)), 128.2 (*d*, C(4)), 56.2 (*d*, C(17)), 56.0 (*d*, C(14)), 53.7 (*d*, C(9)), 42.6 (*s*, C(13)), 39.6 (*t*, C(12)), 39.4 (*t*, C(24)), 39.1 (*t*, C(7)), 38.2 (*s*, C(10)), 36.5 (*t*, C(22)), 36.0 (*t*, C(1)), 35.9 (*d*, C(8)), 35.6 (*t*, C(20)), 28.1 (*d*, C(16)), 28.0 (*d*, C(25)), 25.8 (*t*, C(15)), 24.0 (*t*, C(23)), 23.8 (*t*, C(3)), 22.7 (*q*, C(27)), 22.5 (*q*, C(26)), 21.2 (*t*, C(11)), 19.3 (*q*, C(19)), 18.6 (*q*, C(21)), 18.3 (*t*, C(2)), 11.8 (*q*, C(18)). MS: *m*/*z* = 399 (15.3 %), 383 (68.2 %), 111 (100 %).

Further elution with the same eluent afforded (*E*)-cholest-4-en-6-one oxime (**5**) which after crystallization from acetone gave 0.83 g (80.2 %), m.p. 161–162 ºC (lit.[8] m.p. 163–165 ºC). IR (KBr): 3250, 2935, 1296, 913, 803. ^{1}H-NMR: 0.67 (*s*, 3H, CH_3(18)), 0.86 (*d*, 6H, CH_3(26), CH_3(27)), 0.89 (*d*, 3H,

CH_3(21)), 0.93 (*s*, 3H, CH_3(19)), 3.29 (*dd*, *J* = 3.8, 14.6 1H, H_β–C(7)), 5.86 (*t*, *J* = 3.6, 1H, H–C(4)), 9.63 (*br s*, 1H, =NOH). ^{13}C-NMR: 159.2 (*s*, C(6)), 140.8 (*s*, C(5)), 124.9 (*d*, C(4)), 56.7 (*d*, C(17)), 56.0 (*d*, C(14)), 52.5 (*d*, C(9)), 42.6 (*s*, C(13)), 39.6 (*t*, C(12)), 39.4 (*t*, C(24)), 37.4 (*s*, C(10)), 36.2 (*t*, C(22)), 36.1 (*t*, C(1)), 35.7 (*d*, C(8)), 33.5 (*d*, C(20)), 29.9 (*t*, C(7)), 28.1 (*t*, C(16)), 27.9 (*d*, C(25)), 25.8 (*t*, C(15)), 24.0 (*t*, C(23)), 23.8 (*t*, C(3)), 22.8 (*q*, C(27)), 22.5 (*q*, C(26)), 21.3 (*t*, C(11)), 19.3 (*q*, C(19)), 18.6 (*q*, C(21)), 18.3 (*t*, C(2)), 11.9 (*q*, C(18)). MS: *m*/*z* = 399 (93.2 %), 356 (54.1 %), 110 (100 %).

*Photoisomerization of the (*E*)-oxime **5***

To a solution of oxime **5** (500 mg) and $NH_2OH{\cdot}HCl$ (500 mg) in EtOH (200 ml), pyridine (3.63 ml) was added and the reaction mixture was irradiated with a high pressure mercury lamp (TQ 150 Z2) for 6 h. After evaporation, the obtained oily residue was dissolved in Et_2O, washed with water, dried over $CaSO_4$ and evaporated to dryness. The resulting mixture was chromatographed on SiO_2 (0.040–0.063 mm, 20 g). Elution with *n*-hexane–toluene (6:4) gave cholest-4-en-6-one (**3**) (25 mg, 5 %).

Elution with toluene-EtOAc (97:3) afforded (*Z*)-cholest-4-en-6-one oxime (**4**) (170 mg, 34 %).

Further elution with the same eluent gave unchanged starting (*E*)-oxime **5** (285 mg, 57 %).

Beckmann rearrangement of (Z)*-cholest-4-en-6-one oxime (**4**)*

To a solution of oxime **4** (300 mg) in dioxane (14 ml), thionyl chloride ($SOCl_2$), (0.14 ml) was added. The solution was stirred for 5 min at room temperature. Water was added to this solution, and the reaction mixture was extracted with diethyl ether. The extract was washed with water, 5 % $NaHCO_3$ and water, dried over $CaSO_4$. Removal of the solvent gave a product (270 mg) which was chromatographed on SiO_2 (0.040–0.063 mm, 15 g). Elution with toluene–EtOAc (9:1) gave a complex mixture (20 mg), which was not further investigated.

Elution with toluene–EtOAc (7:3) afforded 7-aza-B-homocholest-4-en-6-one (**6**) (230 mg, 65.7 %), m.p. 136–143 ºC. IR (KBr): 3452, 1663. ^{1}H-NMR: 0.67 (*s*, 3H, CH_3(18)), 0.86 (*d*, 6H, CH_3(26), CH_3(27)), 0.90 (*d*, 3H, CH_3(21)), 1.09 (*s*, 3H, CH_3(19)), 2.84 (*ddd*, *J* = 3.6, 10, 14.2, 1H, H_α–C(7a)), 3.04 (*ddd*, *J* = 1.9, 7.4, 14.6, 1H, H_β–C(7a)), 6.01 (*t*, *J* = 3.6, 1H, H–C(4)), 6.43 (*br s*, W/2 = 12 Hz, 1H, NH). ^{13}C-NMR: 176.8 (*s*, C(6)), 145.1 (*s*, C(5)), 129.4 (*d*, C(4)), 56.2 (*d*, C(17)), 52.9 (*d*, C(14)), 51.4 (*d*, C(9)), 46.8 (*t*, C(7a)), 42.6 (*s*, C(13)), 39.7 (*t*, C(12)), 39.4 (*t*, C(24)), 38.8 (*d*, C(8)), 38.8 (*s*, C(10)), 35.9 (*t*, C(22)), 35.7 (*d*, C(20)), 34.4 (*t*, C(1)), 27.9 (*d*, C(25)), 27.9 (*t*, C(16)), 25.1 (*t*, C(15)), 24.8 (*t*, C(23)), 23.7 (*t*, C(3)), 22.7 (*q*, C(27)), 22.5 (*q*, C(26)), 22.2 (*t*, C(11)), 20.5 (*q*, C(19)), 18.5 (*q*, C(21)), 16.7 (*t*, C(2)), 11.8 (*q*, C(18)). MS: *m*/*z* = 399 (100 %), 384 (10.5 %), 371 (16.3 %), 151 (30.3 %), 123 (36.8 %).

Photoreaction of (Z)*-cholest-4-en-6-one oxime (**4**)*

(a) In methanol. A solution of oxime **4** (300 mg, 0.73 mmol) in methanol (200 ml was flushed with argon, and irradiated under argon with a 6 W low pressure mercury lamp (Applied Photophysics Ltd. G4T5) for 6 h. The reaction mixture was evaporated and the residue chromatographed on SiO_2 (0.040–0.063 mm, 30 g). Elution with toluene afforded the enone **3** (63.3 mg, 21 %).

Elution with toluene–EtOAc (97:3) gave unchanged starting (*Z*)-oxime **4** (74.4 mg, 24.8 %).

Further elution with the same eluent gave (*E*)-oxime **5** (70.3 mg, 23.4 %).

Elution with toluene–EtOAc (7:3), afforded a complex mixture which was rechromatographed to give the lactam **6** (20.3 mg, 6.8 %).

(b) In benzene–glacial acetic acid (94:6). A solution of oxime **4** (150 mg, 0.351 mmol) in benzene-glacial acetic acid (200 ml) was flushed with argon and then irradiated under argon with a 6 W low pressure mercury lamp (Applied Photophysics Ltd. G4T5) for 12 h. The reaction mixture was evaporated to dryness and the residue chromatographed on SiO_2 (0.040–0.063 mm, 25 g). Elution with toluene afforded the enone **3** (25.7 mg, 17.1 %).

Elution with toluene–EtOAc (97:3) gave unchanged starting (*Z*)-oxime **4** (116 mg, 77.3 %).

Further elution with the same eluent gave the (*E*)-oxime **5** (2.1 mg, 1.4 %).

Acknowledgement: The authors acknowledge the financial support of the Ministry of Science, Technology and Development of Serbia. (Part of the project "Synthesis and chemical transformations of steroidal and modified steroidal molecules" - Project No. 1702).

ИЗВОД

ФОТОХЕМИЈСКО И БЕКМАНОВО ПРЕМЕШТАЊЕ (*Z*)-ХОЛЕСТ-4-ЕН-6-ОН ОКСИМА

НАТАЛИЈА М. КРСТИЋ[а], МИРА С. БЈЕЛАКОВИЋ[а], МИЛАН М. ДАБОВИЋ[а], ЉУБИНКА Б. ЛОРЕНЦ[а,б] и ВЛАДИМИР Д. ПАВЛОВИЋ[б,а]

[а]Центар за хемију, ИХТМ, п. пр. 473, 11001 Београд и [б]Хемијски факултет, Универзитет у Београду, Студентски трг 12-16, п. пр. 158, 11001 Београд

Бекманово премештање (*Z*)-холест-4-ен-6-он оксима (**4**) (који је добијен у 4 фазе, полазећи од холест-5-ен-3β-ола (**1**)) са тионил-хлоридом у диоксанском раствору, као једини производ даје лактам енамидног типа, тј., 7-аза-B-хомохолест-4-ен-6-он (**6**). Фотореакцијом истог једињења у метанолу, или у раствору бензен-сирћетна киселина, настаје смеса производа коју чине полазни кетон **3** и производи *Z*/*E* изомеризације, док је лактам **6** добивен у врло ниском приносу (7 %) само у метанолном раствору.

(Примљено 27. новембра 2003)

REFERENCES

1. H. Suginome, K. Ohshima, Y. Ohue, T. Ohki, H. Senboku, *J. Chem. Soc. Perkin Trans 1* (1994) 3239 and references cited therein
2. H Suginome, M. Koji, S. Yamada, *J. Chem. Soc. Perkin Trans. 1* (1988) 321 and references cited therein
3. M. S. Ahmad, N. Z. Kahn, Z. Alan, *J. Chem. Res (S)*, (1985) 191
4. K. Gaši, Z. Sakač, O. Arcson, S. Stanković, B. Ribar, L. Szilagyi, D. Miljković, *J. Serb. Chem. Soc.* **56** (1991) 699
5. C. W. Shoppe, J. K. Hummer, R. E. Lack, P. Raw, S. K. Roy, *Tetrahedron* Supplement No. **7** (1966) 315
6. M. Lj. Mihailović, Lj. Lorenc, V. Pavlović, J. Kalvoda, *Tetrahedron* **33** (1977) 441
7. R. B. Turner, *J. Am. Chem. Soc.* **74** (1952) 5362
8. H. Suginome, M. Koji, T. Ohtsuka, S. Zamada, T. Ohki, H. Senekori, A. Farusaki, *J. Chem. Soc. Perkin Trans. I* (1992) 427.