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Hydride reduction of B-norcholestane 5α,6α-epoxide

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B-Norcholestane epoxide **2** is reduced with lithium aluminium hydride to give either the 3β,6α-diol **3** or the corresponding 3β,5α-diol **4**, depending on the quality of the reducing reagent employed. A plausible mechanistic explanation of the obtained results is suggested.

Keywords: 5α,6α-epoxy-B-norcholestan-3β-yl acetate, 5α-hydroxy-B-norcholestan-3β-yl acetate, 6α-hydroxy-B-nor-5β-cholestan-3β-yl acetate, lithium aluminium hydride, lithium triethylborohydride.

INTRODUCTION

Investigations concerning the epoxidation of the olefinic double bond in Δ^5-unsaturated B-norsteroids (such as **1**, Scheme 1) have shown that this reaction takes place stereoselectively to give as the only stereoisomer the corresponding 5α,6α-epoxides (of type **2**) in high yields of over 90 %.[1–4] However, for the reductive fission of the epoxide ring in these derivatives with lithium aluminium hydride, contradictory results exist in literature.

Thus, Dauben *et al.*[2,5] reported that 5α,6α-epoxy-B-norcholestan-3β-yl acetate (**2**) reacts with lithium aluminium hydride to give a 3,6-diol, which, on the basis of chemical evidence, was characterized as the 3β,6α-A/B *cis*-derivative **3**. On the other hand, Joška *et al.* upon similar reduction of the same substrate with lithium aluminium hydride isolated an isomeric 3,5-diol of the 3β,5α-A/B *trans*-configuration[4] (compound **4**.)**

Since 5-hydroxy-B-nor-5α-cholestan-3β-yl acetate (**7**) was required as the starting material for our study of the oxidative fragmentation of the C(5)–C(10) bond in 5α-alcohols of the B-norsteroid series, it was considered of interest to re-examine the

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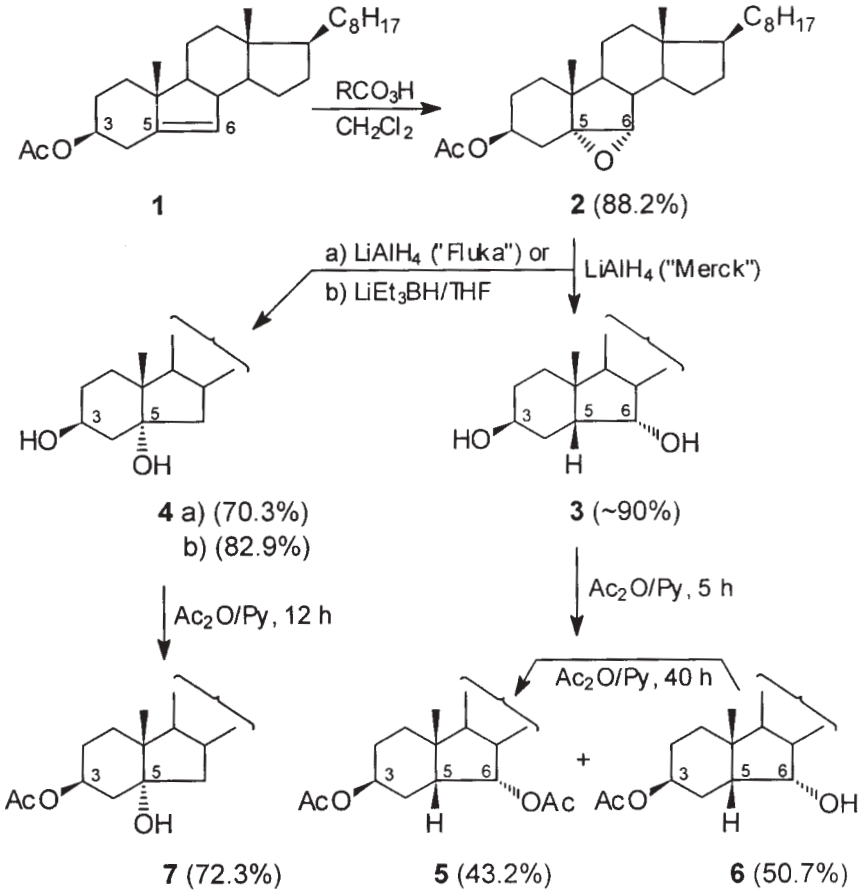
** These authors observed that the reduction of the analogous B-norandrostane 5α,6α-epoxides with lithium aluminium hydride also gives the corresponding 5α-alcohols.[4]



Scheme 1.

lithium aluminium hydride reduction of epoxide **2** with the specific aim: (i) to find out a possible explanation for its different behaviour towards lithium aluminium hydride and (ii) to determine optimal experimental conditions by which the 5α-hydroxy compound, rather than the corresponding 6α-isomer, can be obtained.

In addition, in this paper the spectral characteristics (IR, ^{1}H- and ^{13}C-NMR data) of the prepared compounds, which have not been described in previous studies, are presented and discussed.

RESULTS AND DISCUSSION

5α,6α-Epoxy-B-norcholestan-3β-yl acetate (**2**) was reduced with a large excess of lithium aluminium hydride (produced by Merck) in either diethyl ether or tetrahydrofuran, at reflux until complete consumption of substrate (53 h in the former, and 3 h in the latter solvent). In both cases, the 3β,6α-diol **3** was isolated as the sole reduction product in a high yield of *ca.* 90 % (see Experimental). Diol **3** was acetylated with acetic

anydride in pyridine at room temperature for 5 h to give two products which were separated by column chromatography.

The more mobile component (isolated as an oil in 43.2 % yield) was identified as the 3β,6α-diacetate **5** on the basis of the following evidences. In its IR spectrum the absorption by a free hydroxyl group was absent. The ^{1}H-NMR spectrum showed two singlets for secondary acetate groups at δ 2.00 ppm and δ 2.08 ppm and the signals of the corresponding protons at δ 5.01 ppm and δ 5.30 ppm, respectively. In addition, the number of the primary, secondary, tertiary and H-free C-atoms in the DEPT ^{13}C-NMR spectrum (7 CH_3, 10 CH_2, 9 CH and 4 H-free C atoms) is in complete agreement with structure **5**.

For the more polar component (obtained in 50.7 % yield) the analytical and spectral data (see Experimental) indicated the structure of the diol monoacetate **6**. This compound was subjected to a prolonged acetylation (with acetic anhydride in pyridine at room temperature for 40 h) to give the diacetate **5**.

The 5β-configuration in compounds **5** and **6** was supported by ^{13}C-chemical shifts of their H_3C(19) carbons. The resonances at 23.42 ppm and 23.75 ppm, assigned to H_3C(19) in compounds **5** and **6**, respectively, are characteristic for a 19-methyl group when present in 5β-derivatives of both the natural and B-norsteroid series.[6] However, the configuration at C(6) was deduced from the ^{1}H-NMR spectral parameters observed for the C(6) proton in these compounds. In **5** the signal appears at δ 5.30 ppm as *dd*, J = 5.2, 3.8 Hz, and in **6** at δ 3.98 ppm as *ft*, J = 3.6 Hz. Thus, in both cases the coupling constants between the C(6) proton and the vicinal C(5) and C(8) protons correspond to a dihedral angle which is less than 50º,[7] thus indicating the existence of 6β-oriented hydrogen in these compounds.

In a repeat experiment the epoxide **2** was reduced (in tetrahydrofuran at reflux for 48 h) with lithium aluminium hydride produced by Fluka. In this case, to our great surprise, the 3β,5α-diol **4** was obtained as the only reaction product (in *ca*. 70 % yield). It was identified by its melting point (which was identical to the one reported by Joška *et al.*[4] for diol **4**) and its structure was substantiated by the spectral characteristics presented in the Experimental.

The same 3β,5α-diol **4** was obtained (in about 83 % yield) when the reduction of epoxide **2** was performed with lithium triethylborohydride in tetrahydrofuran at reflux for 24 h.

After acetylation (with acetic anhydride in pyridine) diol **4** was transformed to diol monoacetate **7**. Its structure was confirmed by spectral analysis, *i.e.,* the IR (absorptions between 3560–3450 cm^{-1} for the hydroxyl group and at 1712 and 1270 cm^{-1} for the acetoxyl group), ^{1}H-NMR (singlet at δ 2.02 ppm for AcO group and multiplet at δ 5.23 ppm for the corresponding C(3) proton), and ^{13}C-NMR spectral data (singlet at 84.12 ppm for the hydroxylated C(5) carbon and quartet at 15.92 ppm for the H_3C(19) carbon).

The ^{13}C-NMR chemical shifts of selected carbons of the B-norsteroid derivatives **2** and **4**–**7** are listed in Table I.

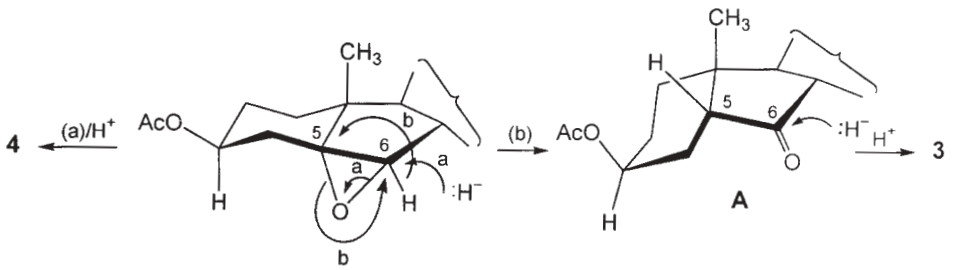
A comparison of the data for the H_3C(19) signals of the 5α- and the 5β-B-norsteroidal compounds indicates that in the 5α-derivatives, due to the shielding interaction of the C(2)–Hβ bond with the H_3C(19) group, the C(19) signal is shifted upfield with respect to

the C(19) signal in the 5β-B-norcompounds. Therefore, the stereochemistry of the A/B ring junction in the modified B-norsteroids can be deduced from the C-19 shielding, as was previously observed for compounds of the natural 5α- and 5β-series.[6]

TABLE I. Selected ^{13}C-NMR chemical shifts [ppm] of **2** and **4**–**7** in $CDCl_3$ solution

Carbon	**2**	**4**	**5**	**6**	**7**
C(1)	30.9 *t*	30.1 *t*	33.6 *t*	33.8 *t*	27.3 *t*
C(2)	26.9 *t*	27.5 *t*	26.6 *t*	26.7 *t*	25.9 *t*
C(3)	72.1 *d*	68.3 *d*	70.0 *d*	71.1 *d*	71.7 *d*
C(4)	31.1 *t*	40.4 *t*	26.1 *t*	26.4 *t*	39.7 *t*
C(5)	68.3 *s*	84.9 *s*	43.7 *d*	45.6 *d*	84.1 *s*
C(6)	60.3 *d*	39.6 *t*	77.4 *d*	75.7 *d*	36.8 *t*
C(8)	42.3 *d*	38.7 *d*	47.0 *d*	48.3 *d*	38.7 *d*
C(9)	48.0 *d*	52.8 *d*	49.9 *d*	49.8 *d*	52.6 *d*
C(10)	38.7 *s*	45.1 *s*	38.7 *s*	38.7 *s*	45.1 *s*
C(18)	12.0 *q*	12.5 *q*	12.0 *q*	12.1 *q*	12.5 *q*
C(19)	15.3 *q*	16.0 *q*	23.4 *q*	23.7 *q*	15.9 *q*

The obtained results show that the manner in which the B-norcholestane epoxide **2** reacts with lithium aluminium hydride is highly dependent upon the quality of the reducing agent used.



Scheme 2.

It is known that, in general, the reduction of an epoxide ring with lithium aluminium hydride (which proceeds by S_N2 nucleophilic substitution by hydride ion) takes place at the least substituted carbon atom to give the more substituted alcohol. In this case the "normal" reaction course, *i.e.*, hydride attack at the less substituted C(6) position of epoxide **2** (path (a), Scheme 2), gives finally the 3β,5α-diol **4**. However, the "reversed reduction", leading to the 3β,6α-diol **3**, requires a different mechanistic pathway. It can be safely assumed that some impurity (probably a salt) present in traces in the reducing reagent can act as a Lewis acid# to induce hydride shift from the C(6) to the

On the basis of the present data it is still uncertain which species can act as a Lewis catalyst. Preliminary experiments in which reductions were performed in the presence of catalytic amounts of $AlCl_3$ and LiCl, respectively, have shown that the former salt induces a skeletal rearrangement in epoxide **2**,[5] while the latter salt was without effect on the reaction course.

C(5) position (path (b), Scheme 2) producing the carbonyl intermediate **A** which is further reduced (from the less hindered β-side) to give the 3β,6α-diol **3**.#

The different behaviour of the 5α,6α-B-nor epoxide **2** in reductions performed with lithium aluminium hydride of various qualities (not observed in similar reactions of the natural steroid 5α,6α-epoxides) is probably due to the strain which exists in its B-ring moiety. Therefore, if it is required that a diol of type **4** (starting from the corresponding epoxide) be prepared, reduction with lithium triethylborohydride is recommended.

EXPERIMENTAL

General

Column chromatography: silica gel 0.040–0.063 mm. TLC: silica gel G (Stahl), detection with 50 % aq. H_2SO_4 soln. M.ps.: uncorrected. IR Spectra: Perkin-Elmer-337 spectrophotometer; ν in cm^{-1}. NMR Spectra: Varian Gemini 200(^1H at 200, ^{13}C at 50 MHz); $CDCl_3$ soln. at r.t.; $SiMe_4$ as internal standard: δ in ppm, *J* in Hz. Mass spectra: Finnigan-MAT 8230; *m*/*z* (rel. intensity in %); ionization energy 70 eV.

*B-Norcholest-5-en-3*β*-yl acetate (**1**)*[9,10]

M.p. 76–77 ºC (from MeOH) (lit.[11] m.p.77–79 ºC). IR (KBr): 1729, 1243, ^1H-NMR: 0.67 (*s*, Me(18)), 0.85 (*s*, Me(19)), 2.04 (*s*, AcO), 4.64 (*m*, H-C(3)), 5.39 (*fs*, H-C(6)). ^{13}C-NMR: 170.5 (*s*, CH_3COO), 147.6 (*s*, C(5)), 126.4 (*d*, C(6)), 73.7 (*d*, C(3)), 62.3 (*d*, C(9)), 55.7 (*d*, C(17)), 54.3 (*d*, C(14)), 46.1 (*d*, C(8)), 44.8 (*s*, C(10)), 44.4 (*s*, C(13)), 40.0 (*t*, C(12)), 39.4 (*t*, C(24)), 36.9 (*t*, C(1)), 36.2 (*t*, C(22)), 35.6 (*d*, C(20)), 32.7 (*t*, C(4)), 28.5 (*t*, C(16)), 27.9 (*d*, C(25)), 27.9 (*t*, C(2)), 24.2 (*t*, C(15)), 23.8 (*t*, C(23)), 22.8 (*q*, C(27)), 22.5 (*q*, C(26)), 21.3 (*q*, CH_3COO), 21.1 (*t*, C(11)), 18.7 (*q*, C(21)), 14.9 (*q*, C(19)), 12.2 (*q*, C(18)).

*5*α*,6*α*-Epoxy-B-norcholestan-3*β*-yl acetate (**2**)*

To a stirred solution of **1** (11.10 g, 26.81 mmol) in CH_2Cl_2 (400 ml) *m*-chloroperbenzoic acid (assay 70 %) (6.90 g, 27.99 mmol) was added, and the mixture left at room temperature for 1 h. The mixture was washed with aq. Na_2SO_3 solution, aq. $NaHCO_3$ solution and water, dried over Na_2SO_4 and evaporated *in vacuo* to afford the epoxide **2**, which was recrystallized from MeOH (10.17 g, 88.2 %). M.p. 110–112 ºC (lit.[4] m.p. 111–112 ºC). IR (KBr): 1729, 1383, 1375, 1365, 1247, 1033. ^1H-NMR: 0.63 (*s*, Me(18)), 0.85 (*s*, Me(19)), 2.03 (*s*, AcO), 3.26 (*s*, H-C(6)), 4.98 (*m*, H-C(3)). ^{13}C-NMR: 170.2 (*s*, CH_3COO), 72.1 (*d*, C(3)), 68.3 (*s*, C(5)), 60.3 (*d*, C(6)), 55.5 (*d*, C(17)), 50.5 (*d*, C(14)), 48.0 (*d*, C(9)), 44.3 (*s*, C(13)), 42.3 (*d*, C(8)), 39.6 (*t*, C(12)), 39.4 (*t*, C(24)), 38.7 (*s*, C(10)), 36.1 (*t*, C(22)), 35.6 (*d*, C(20)), 31.1 (*t*, C(4)), 30.9 (*t*, C(1)), 28.5 (*t*, C(16)), 27.9 (*d*, C(25)), 26.9 (*t*, C(2)), 24.1 (*t*, C(15)), 23.8 (*t*, C(23)), 22.7 (*q*, C(27)), 22.5 (*q*, C(26)), 21.2 (*q*, CH_3COO), 20.8 (*t*, C(11)), 18.6 (*q*, C(21)), 15.3 (*q*, C(19)), 12.0 (*q*, C(18)). MS (CI): 431 ($M^+ + 1$), 353 (431–60–18, 100 %).

*Reduction of the epoxide **2** with lithium aluminium hydride (Merck)*

(i) *In diethyl ether* – The epoxide **2** (2.0 g) was dissolved in dry Et_2O (100 ml) and reduced with $LiAlH_4$ (Merck) (1.5 g) in the usual way. After heating at reflux for 53 h, water was added until a thick white precipitate formed. The organic layer was washed with water, dried (Na_2SO_4), and evaporated *in vacuo* to dryness to give 3β,6α-diol **3** (1.7 g, 93.92 %), m.p. 142–143 ºC (lit.[4] m.p. 143–144 ºC).

(ii) *In tetrahydrofuran (THF)* – The epoxide **2** (0.60 g) in dry THF (30 ml) was reduced with $LiAlH_4$ (Merck) (0.49 g) by heating at reflux for 3 h. The mixsture was worked up in the usual manner to give diol **3** (0.49 g, 90.04 %). M.p. 142–144 ºC (MeOH) (lit.[4] m.p. 143–144 ºC).

A similar explanation for "reversed reduction" of some aliphatic epoxides with "mixed hydride" ($LiAlH_4$-$AlCl_3$) is suggested by Eliel and Rerick.[8]

Acetylation of diol **3**

The diol **3** was acetylated with Ac_2O (12 ml) in dry pyridine (12 ml) at room temperature for 5 h. The usual work-up gave a residue (1.9 g) which was chromatographed on a SiO_2 column (100 g). Elution with toluene/EtOAc (95:5) gave 0.95 g (43.18 %) of pure 3β,6α-diacetate **5** as an oil. IR (neat): 1734, 1715, 1265, 1030. ^{1}H-NMR: 0.64 (*s*, Me(18)), 0.85 (*s*, Me(19)), 0.88 and 0.94 (two *d*, Me(26) and Me(27)), 2.00 (*s*, AcO-C(3)), 2.08 (*s*, AcO-C(6)), 5.01 (*m*, H-C(3)), 5.30 (*dd*, *J* 3.8, 5.2, H-C(6)). ^{13}C-NMR: 170.49 (*s*, CH_3COO–C(3)), 170.42 (*s*, CH_3COO–C(6)), 77.44 (*d*, C(6)), 69.95 (*d*, C(3)), 55.41 (*d*, C(17)), 52.91 (*d*, C(14)), 49.89 (*d*, C(9)), 46.99 (*d*, C(8)), 44.17 (*s*, C(13)), 43.74 (*d*, C(5)), 39.31 (*t*, C(24)), 39.13 (*t*, C(12)), 38.67 (*s*, C(10)), 36.05 (*t*, C(22)), 35.47 (*d*, C(20)), 33.58 (*t*, C(1)), 28.30 (*t*, C(16)), 27.84 (*d*, C(25)), 26.55 (*t*, C(2)), 26.13 (*t*, C(4)), 23.87 (*t*, C(15)), 23.67 (*t*, C(23)), 23.42 (*q*, Me(19)), 22.65 (*q*, Me(27)), 22.40 (*q*, Me(26)), 21.65 (*t*, C(11)), 20.94 and 21.20 (two *q*, CH_3COO), 18.63 (*q*, Me(21)), 11.97 (*q*, Me(18)).

Further elution with the same toluene/EtOAc (95:5) mixture gave 3β-acetoxy-B-nor-5β-cholestan-6α-ol (**6**) (1.02 g, 50.74 %). M.p. 72–73 ºC (lit.[4] m.p. 77–79 ºC). IR (neat): 3441, 1703, 1273. ^{1}H-NMR: 0.65 (*s*, Me(18)), 0.85 (*s*, Me(19)), 0.88 and 0.91 (two *d*, Me(26) and Me(27)), 2.02 (*s*, AcO), 3.98 (*ft*, *J* 3.6, H-C(6)), 5.12 (*m*, H-C(3)). ^{13}C-NMR: 170.93 (*s*, CH_3COO), 75.71 (*d*, C(6)), 71.08 (*d*, C(3)), 55.55 (*d*, C(14)), 51.80 (*d*, C(17)), 49.76 (*d*, C(9)), 48.29 (*d*, C(8)), 45.59 (*d*, C(5)), 43.79 (*s*, C(13)), 39.44 (two *t*, C(12) and C(24)), 38.66 (*s*, C(10)), 36.18 (*t*, C(22)), 35.63 (*d*, C(20)), 33.85 (*t*, C(1)), 28.57 (*t*, C(16)), 27.95 (*d*, C(25)), 26.71 (*t*, C(2)), 26.40 (*t*, C(4)), 23.85 (*t*, C(23)), 23.75 (*q*, Me(19)), 23.75 (*t*, C(15)), 22.76 (*q*, Me(27)), 22.51 (*q*, Me(26)), 21.87 (*t*, C(11)), 21.49 (*q*, CH_3COO), 18.70 (*q*, Me(21)), 12.15 (*q*, Me(18)). MS (CI):433 ($M^+ + 1$, 1 %), 355 (433–60–18, 100 %).

When the dihydroxy derivative **3** was acetylated with Ac_2O in pyridine for 40 h, only the oily diacetate **5** was obtained.

*Acetylation of 3β-acetoxy-B-nor-5β-cholestan-6α-ol (**6**)*

The monoacetate **6** was acetylated with Ac_2O in pyridine at room temperature for 40 h. The usual work-up gave the oily diacetate **5**.

*Reduction of the epoxide **2** with lithium aluminium hydride (Fluka)*

The epoxide **2** (2.00 g) was reduced with $LiAlH_4$ (Fluka) (2.00 g) in dry THF (70 ml) at reflux for 48 h. The reaction mixture was worked up as usually. The crude 3β,5α-diol **4** (1.43 g) was crystallized from methanol to give 1.27 g (70.3 %) of diol **4**. M.p. 139–140 ºC (lit.[4] m.p. 138–139 ºC). ^{1}H-NMR: 0.66 (*s*, Me(18)), 0.85 (*s*, Me(19)), 0.87 and 0.88 (two *d*, Me(26) and Me(27)), 0.91 (*d*, Me(21)), 4.16 (*m*, H-C(3)), ^{13}C-NMR: 84.88 (*s*, C(5)), 68.28 (*d*, C(3)), 56.61 (*d*, C(17)), 55.77 (*d*, C(14)), 52.84 (*d*, C(9)), 45.07 (two *s*, C(10) and C(13)), 40.39 (*t*, C(4)), 40.15 (*t*, C(12)), 39.59 (*t*, C(6)), 39.44 (*t*, C(24)), 38.75 (*d*, C(8)), 36.16 (*t*, C(22)), 35.63 (*d*, C(20)), 30.08 (*t*, C(1)), 28.39 (*t*, C(16)), 27.93 (*d*, C(25)), 27.46 (*t*, C(2)), 24.40 (*t*, C(15)), 23.78 (*t*, C(23)), 22.76 (*q*, C(27)), 22.51 (*q*, C(26)), 21.69 (*t*, C(11)), 18.68 (*q*, C(21)), 16.02 (*q*, C(19)), 12.53 (*q*, C(18)).

*Reduction of the epoxide **2** with lithium triethylborohydride*

The epoxide **2** (2.00 g, 4.6 mmol) was dissolved in dry THF (10 ml) and $LiEt_3BH$ (6 ml of 1 *m* solution, 6 mmol) was added to the solution. The mixture was heated at reflux with stirring for 24 h. Additional amount of $LiEt_3BH$ (6 ml, 6 mmol) was added, and the heating at reflux continued for 24 h. The mixture was cooled to room temperature, and water (2–3 ml) was added dropwise to hydrolyze the mixture. The reaction mixture was diluted with Et_2O and washed with water, dried over Na_2SO_4, filtered, and evaporated to dryness. The crude product was crystallized from MeOH to yield 1.50 g (82.87 %) of 3β,5α-diol **4**.

Acetylation of 5-hydroxy-B-nor-5α-cholestan-3β-yl-acetate (**4**)

The diol **4** (1.50 g) was acetylated with Ac_2O (10 ml) in pyridine (12 ml) for 12 h. Working up and crystallization from MeOH afforded 1.20 g (72.29 %) of the 3β-acetate **7**, m.p. 121–122 ºC (lit.[4]

m.p. 121–122 ºC). IR (KBr): 3557, 1714, 1260. ^{1}H-NMR: 0.65 (*s*, Me(18)), 0.85 (*s*, Me(19)), 0.87 (*d*, Me(26)), Me(27)), 0.91 (*d*, Me(21)), 2.02 (*s*, AcO), 5.23 (*m*, H-C(3)). ^{13}C-NMR: 170.73 (*s*, CH_3COO), 84.12 (*s*, C(5)), 71.70 (*d*, C(3)), 56.44 (*d*, C(17)), 55.75 (*d*, C(14)), 52.62 (*d*, C(9)), 45.07 (two *s*, C(10) and C(13)), 40.09 (*t*, C(12)), 39.70 (*t*, C(4)), 39.46 (*t*, C(24)), 38.73 (*d*, C(8)), 36.80 (*t*, C(6)), 36.18 (*t*, C(22)), 35.67 (*d*, C(20)), 28.41 (*t*, C(16)), 27.95 (*d*, C(25)), 27.30 (*t*, C(1)), 25.88 (*t*, C(2)), 24.42 (*t*, C(15)), 23.80 (*t*, C(23)), 22.76 (*q*, C(27)), 22.53 (*q*, C(26)), 21.63 (*q*, CH_3COO), 21.43 (*t*, C(11)), 18.70 (*q*, C(21)), 15.92 (*q*, C(19)), 12.53 (*q*, C(18)). MS (CI): 433 ($M^+ + 1$, 1 %), 415 (433–18, 15 %), 355 (433–60–18, 100 %).

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И З В О Д

ХИДРИДНА РЕДУКЦИЈА B-НОРХОЛЕСТАН-5α,6α-ЕПОКСИДА

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Редукцијом B-норхолестан-епоксида **2** помоћу литијум-алуминијум-хидрида добијени су одговарајући 3β,6α-диол **3** или 3β,5α-диол **4**, у зависности од квалитета употребљеног редукционог реагенса. Предложено је вероватно механистичко тумачење добијених резултата.

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