7-METHANESULFONYLOXY-3α,5-CYCLO-5α-CHOLESTANES*

Ladislav KOHOUT

Institute of Organic Chemistry and Biochemistry,
Czechoslovak Academy of Sciences, 166 10 Prague 6

Received June 15, 1988
Accepted July 27, 1988

Acetolysis and hydrogenolysis of 7-methanesulfonyloxy-3α,5-cyclo-5α-cholestanes was studied. The 7β-methanesulfonyloxy derivative *VI* is hydrogenolyzed more readily than its 7α-isomer *III*. The acetolysis gives products of elimination, substitution and rearrangement with participation of the cyclopropane ring. Whereas the 7α-derivative *III* predominantly reacts with elimination, the 7β-derivative *VI* is more susceptible to the participation reaction.

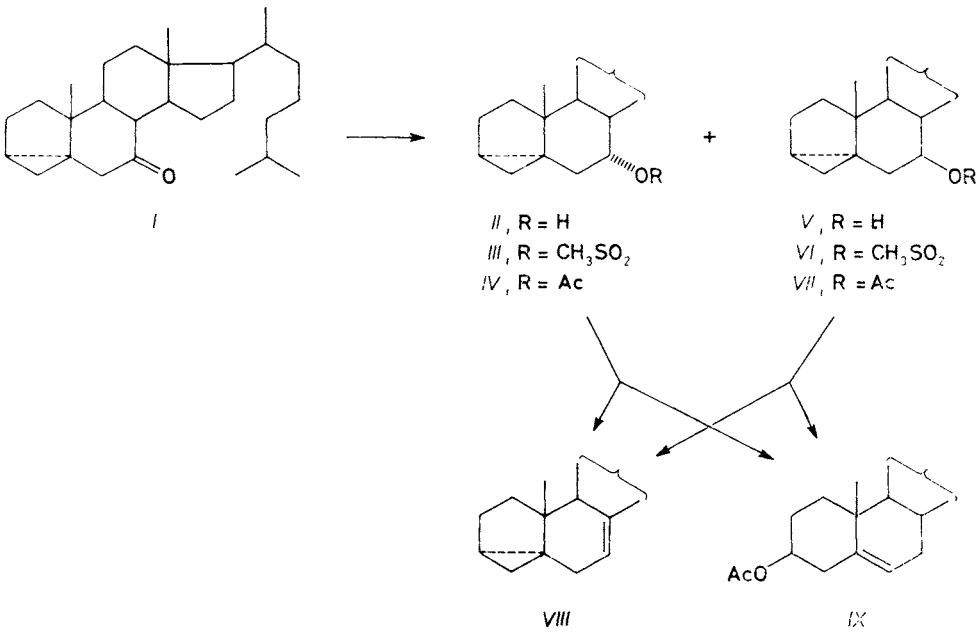
Within the framework of our studies on cyclopropane ring participation in S_N2 reactions[1] we were interested in the behaviour of 7-methanesulfonyloxy derivatives of 3α,5-cyclo-5α-cholestane (*III* and *VI*) under conditions of acetolysis (potassium acetate in acetic acid and acetic anhydride) and hydrogenolysis (lithium aluminium hydride, zinc).

As the starting material we used 3α,5-cyclo-5α-cholestan-7-one (*I*; ref.[2]) which was reduced with lithium aluminium hydride to give a mixture of both the 7-alcohols with the 7α-isomer *II* slightly predominating. Use of lithium tri-tert-butoxyaluminium hydride in the reduction enhanced substantially the predominance of the 7α-alcohol in the reaction mixture. Both the 7-alcohols *II* and *V* were oxidized with Jones reagent to give the starting ketone, showing thus that the 3α,5-cyclo system remains intact under the reaction conditions. Reaction with methanesulfonyl chloride in pyridine afforded the corresponding methanesulfonyloxy derivatives *III* and *VI*, however, mesylation of the 7α-alcohol *II* was accompanied by formation of an olefin. This olefin contained a cyclopropane ring (IR spectrum: 3 055 cm^{-1}, ^1H NMR spectrum: two multiplets in the region −0·12 to 0·21 and 0·29 to 0·48 ppm) and a double bond bearing only one proton (IR spectrum: 3 020 and 1 673 cm^{-1}, ^1H NMR spectrum: a multiplet at 5·16 ppm), which was consistent with the structure *VIII* (3α,5-cyclo-5α-cholest-7-ene).

Acetolysis of methanesulfonyloxy derivatives *III* and *VI* afforded products listed in Table I. The 7α-methanesulfonyloxy derivative *III* reacted with elimination of the

* Part CCCXL in the series On Steroids; Part CCCXXXIX: Collect. Czech. Chem. Commun. *54*, 1019 (1989).

methanesulfonyloxy group as well as with rearrangement into 5-cholesten-3β-ol acetate (*IX*). The formation of *IX* can be explained by reaction via ions *X* and *XI*. A similar rearrangement with participation of the cyclopropane ring was observed[3] by us e.g. in the acetolysis of 3β-methanesulfonyloxy-5,7α-cyclo-B-homo-5α-cholestane (*XII*) which under similar conditions afforded 7β-acetoxy-B-homo-4-cholestene (*XIII*).



Acetolysis of the 7β-methanesulfonyloxy derivative *VI* was, moreover, accompanied by formation of 7β-acetoxy-3α,5-cyclo-5α-cholestane (*VII*) as an S_N2 reaction product.

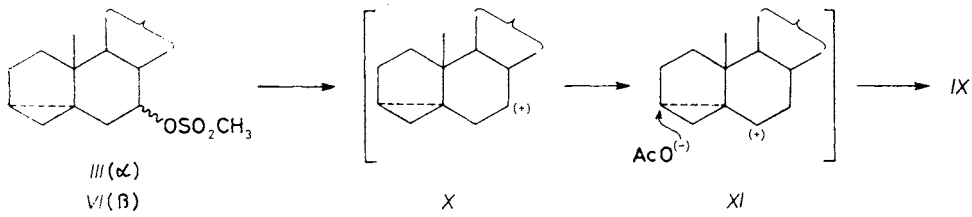
Further, we studied the reactivity of the methanesulfonyloxy group in the reduc-

TABLE I

Yields (%) of products in acetolysis of methanesulfonyloxy derivatives *III* and *VI*

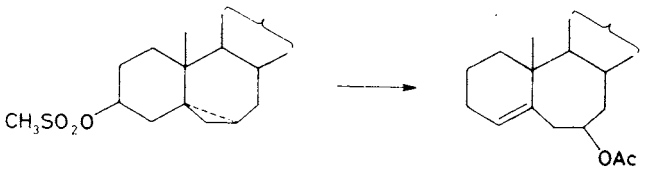
Products	7α-Isomer *III*	7β-Isomer *VI*
Olefin *VIII*	68	12
Acetate *IX*	14	39
Acetate *VII*	—	41

tion with lithium aluminium hydride or with zinc and sodium iodide. In the hydride reduction, both the methanesulfonyloxy derivatives afforded a mixture consisting of the hydrogenolysis product *XIV* and the corresponding alcohol, i.e. *II* from *III* and *V* from *VI*.

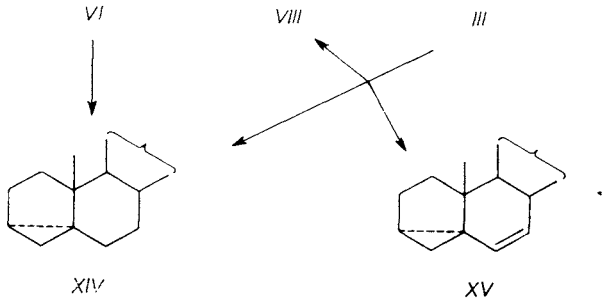


III (α)
VI (β)
X
XI

The reaction of 7β-methanesulfonyloxy derivative *VI* with sodium iodide and zinc resulted in hydrogenolysis of the sulfonyl group under formation of 3α,5-cyclo-5α--cholestane *XIV*, whereas the 7α-isomer *III* afforded a mixture of three compounds which, in addition to the hydrogenolysis product *XIV*, contained two olefins: the above-described 7,8-olefin *VIII* and another olefin which contained a cyclopropane ring and a double bond (IR spectrum: 737 cm^{-1}) with two protons attached (^1H NMR spectrum: two doublets of doublets at 5·17 and 5·52 ppm, geminal J = 10 Hz). The compound was thus 3α,5-cyclo-5α-cholest-6-ene (*XV*).



XII
XIII



XIV
XV

We may conclude that the solvolysis of 7-methanesulfonyloxy-3α,5-cyclo-5α--cholestanes *III* and *VI* proceeds analogously to the solvolysis of the previously studied systems, i.e. under formation of products of substitution, elimination and cyclopropane ring participation, the 7β-methanesulfonyloxy derivative *VI* being more prone to rearrangement. The reductive removal of the methanesulfonyloxy group proceeds more readily with the 7β-derivative *VI*.

EXPERIMENTAL

The melting points were determined on a Kofler block and are uncorrected. Optical rotations were measured in chloroform (unless stated otherwise); error ±3°. Infrared spectra were recorded in tetrachloromethane (unless stated otherwise) on a Zeiss UR 20 spectrometer, wavenumbers are given in cm^{-1}. ^1H NMR spectra were taken on a Tesla BS 497 instrument (100 MHz) in deuterochloroform with tetramethylsilane as internal standard, unless stated otherwise. Chemical shifts are given in ppm (δ-scale), coupling constants (J) and multiplet half-widths ($W_{1/2}$) in Hz. The spectra were interpreted as spectra of the first order. Mass spectra were measured on a ZAB-EG spectrometer (ionizing electron energy 70 eV).

The identity of the prepared samples was checked by mixture melting points, thin-layer chromatography (TLC), IR and ^1H NMR spectra. Preparative TLC was performed on 200 × 200 mm plates with a 0·7 mm thick layer of silica gel (Woelm DC).

The expression "usual work-up" denotes washing with 5% hydrochloric acid, water, 5% aqueous solution of potassium hydrogen carbonate and water, drying over sodium sulfate, filtration and evaporation of the solvent in vacuo. The light petroleum used was a fraction boiling in the range 40—62°C.

3α,5-Cyclo-5α-cholestan-7one (*I*)

A) From 3α,5-*cyclo*-5α-*cholestan*-7α-*ol* (II). Jones reagent was added to a solution of alcohol *II* (138 mg) in acetone (10 ml) to a constant brown colouration. The mixture was set aside at room temperature for 5 min, methanol (1 ml) was added and, after standing for 5 min, the reaction mixture was poured into water. The product was extracted with ether and worked up in the usual manner. The residue (130 mg) was crystallized from methanol to give 91 mg of ketone *I*, m.p. 87—89°C, $[\alpha]_D^{20}$ −4° (*c* 1·1), in agreement with the reported[3] values.

B) From 3α,5-*cyclo*-5α-*cholestan*-7β-*ol* (V). Alcohol *V* (25 mg) was oxidized in the same manner as described under *A*). Crystallization of the crude product (25 mg) afforded 12 mg of ketone *I*, m.p. 85—86°C.

3α,5-Cyclo-5α-cholestan-7α-ol (*II*)

A) By reduction of 3α,5-*cyclo*-5α-*cholestan*-7-*one* (I) *with lithium aluminium hydride.* Lithium aluminium hydride powder (0·8 g) was added to a solution of ketone I (450 mg) in tetrahydrofuran (10 ml). After standing for 10 min, the excess hydride was decomposed with ethyl acetate and methanol. The mixture was poured into water, the product was taken up in ether and worked up as usual. The residue (450 mg) consisted (according to TLC) of two compounds (*II* and *V*) in approximately 1 : 1 ratio. They were separated by chromatography on a column of silica gel (50 g) in light petroleum–ether (33 : 1). Fractions, containing the more lipophilic product, gave 225 mg of alcohol *II*, m.p. 70—73°C (methanol), $[\alpha]_D^{20}$ +52° (*c* 1·7). ^1H NMR spectrum:

−0·05 dd, 1 H (J = 5 Hz, J' = 3 Hz) and 0·33 t (J = 3 Hz) (two cyclopropane protons); 0·69 s, 3 H (3 × H-18); 0·86 d, 6 H (3 × H-26 and 3 × H-27, J = 6); 0·91 s, 3 H (3 × H-19); 0·92 d, 3 H (3 × H-21, J = 5); 3·76 m, 1 H (H-7β, $W_{1/2}$ = 7). IR spectrum: 3 620, 1 040 (OH), 3 065 (cyclopropane). For $C_{27}H_{46}O$ (386·6) calculated: 83·87% C, 11·99% H; found: 83·37% C, 11·74% H.

B) By reduction of 3α,5-*cyclo*-5α-*cholestan*-7-*one* (I) *with lithium tri-tert-butoxyaluminium hydride.* Lithium tri-tert-butoxyaluminium hydride (2 g) was added to a solution of ketone *I* (1 g) in tetrahydrofuran (30 ml). After standing at room temperature for 1 h, the mixture was carefully poured into water and the product was extracted with ether. After the usual work-up, the residue, which (according to TLC) contained two compounds (*II* and *V*), was chromatographed on a column of silica gel (100 g) in light petroleum–ether (30 : 1). Yield 710 mg of alcohol *II*, m.p. 72–74°C (acetone), $[\alpha]_D^{20}$ +51° (*c* 1·1).

C) From 3α,5-*cyclo*-5α-*cholestan*-7α-*ol methanesulfonate* (III). Further chromatographic fractions in the preparation of compound *XIV* (procedure *B*) afforded 680 mg of product which on crystallization from methanol gave 405 mg of alcohol *II*, m.p. 71–73°C, $[\alpha]_D^{20}$ +52° (*c* 1·1).

3α,5-Cyclo-5α-cholestan-7α-ol Methanesulfonate (*III*)

Work-up of TLC zones containing the more polar product in the preparation of olefin *VIII* (procedure *A*) and crystallization of the residue (0·6 g) from methanol afforded 0·42 g of the methanesulfonate *III*, m.p. 91–93°C, $[\alpha]_D^{20}$ +7° (*c* 1·4). ^{1}H NMR spectrum: −0·10–0·20 m, 1 H and 0·30–0·45 m, 1 H (two cyclopropane protons); 0·67 s, 3 H (3 × H-18); 0·85 d, 6 H (3 × H-26 and 3 × H-27, J = 6); 0·90 s, 3 H (3 × H-19); 0·91 d, 3 H (3 × H-21, J = 6); 2·96 s, 3 H (methanesulfonate); 4·87 m, 1 H (H-7β, $W_{1/2}$ = 6). IR spectrum: 3 060, 3 025 (cyclopropane), 1 345, 1 277, 908 (methanesulfonate). For $C_{28}H_{48}O_3S$ (464·8) calculated: 72·36% C, 10·41% H, 6·90% S; found :71·90% C, 10·15% H, 6·82% S.

3α,5-Cyclo-5α-cholestan-7α-ol Acetate (*IV*)

Acetic anhydride (3 ml) was added to a solution of alcohol *II* (350 mg) in pyridine (5 ml). After standing at room temperature overnight, the mixture was poured into water, the product was extracted with ether and processed in the usual manner. The residue was purified by chromatography on a column of silica gel (50 g) in light petroleum–ether (49 : 1). The obtained product (380 mg) was crystallized from methanol to give 247 mg of acetate *IV*, m.p. 73–74°C, $[\alpha]_D^{20}$ +4° (*c* 0·7). ^{1}H NMR: spectrum: −0·20 to −0·01 m, 1 H and 0·16–0·34 m, 1 H (two cyclopropane protons); 0·67 s, 3 H (3 × H-18); 0·85 d, 6 H (3 × H-26 and 3 × H-27, J = 6); 0·89 d, 3 H (3 × H-21, J = 6); 0·91 s, 3 H (3 × H-19); 2·02 s, 3 H (CH_3COO); 4·82 m, 1 H (H-7β, $W_{1/2}$ = 6). IR spectrum: 3 060, 3 025 (cyclopropane), 1 737, 1 251, 1 031 (acetate). For $C_{29}H_{48}O_2$ (428·7) calculated: 81·25% C, 11·29% H; found: 81·30% C, 11·28% H.

3α,5-Cyclo-5α-cholestan-7β-ol (*V*)

A) By reduction of 3α,5-*cyclo*-5α-*cholestan*-7-*one* (I) *with lithium aluminium hydride.* Fractions containing the polar product, in the preparation of alcohol *II* (procedure *A*) afforded 200 mg of noncrystalline alcohol *V*, $[\alpha]_D^{20}$ +33° (*c* 4·4). ^{1}H NMR spectrum: 0·03 dd, 1 H (J = 5; J' = = 7·5) and 0·35 dd, 1 H (J = 3·5; J' = 5) (two cyclopropane protons); 0·69 s, 3 H (3 × H-18); 0·86 d, 6 H (3 × H-26 and 3 × H-27, J = 5·5); 0·91 s, 3 H (3 × H-19); 0·92 d, 3 H (3 × H-21, J = 5); 3·35 m 1 H (H-7α, $W_{1/2}$ = 22). IR spectrum: 3 620, 1 228, 1 021 (hydroxyl), 3 065,

3 020 (cyclopropane). For $C_{27}H_{46}O$ (386·6) calculated: 83·87% C, 11·99% H; found: 82·69% C, 11·46% H.

B) By reduction of 3α,5-*cyclo*-5α-*cholestan*-7-*one* (I) *with lithium tri-tert-butoxyaluminium hydride.* Fractions, containing the polar product, in the preparation of alcohol *II* (procedure *B*) gave 130 mg of alcohol *V*, $[\alpha]_D^{20}$ +37° (*c* 1·1).

C) From 3α,5-*cyclo*-5α-*cholestan*-7β-*ol methanesulfonate* (VI). Work-up of TLC zones, containing polar compound, in the preparation of compound *XIV* (procedure *D*) furnished 135 mg of alcohol *V*, $[\alpha]_D^{20}$ +33° (*c* 1·2).

3α,5-Cyclo-5α-cholestan-7β-ol Methanesulfonate (*VI*)

Methanesulfonyl chloride (1 ml) was added to a solution of alcohol *V* (0·85 g) in pyridine (5 ml). After standing at room temperature for 20 h, the mixture was poured into water, the product was extracted with ether and worked up in the usual manner. The residue (840 mg) was crystallized from methanol to give 560 mg of product *VI*, m.p. 116–118°C, $[\alpha]_D^{20}$ +71° (*c* 0·9). ^{1}H NMR spectrum: 0·04–0·48 m, 2 H (cyclopropane protons); 0·68 s, 3 H (3 × H-18); 0·85 d, 6 H (H-26 and H-27, J = 6); 0·90 s, 3 H (3 × H-19); 0·91 d, 3 H (3 × H-21, J = 6); 2·94 s, 3 H (methanesulfonate); 4·50 m, 1 H (H-7α, $W_{1/2}$ = 28). IR spectrum: 3 065 (cyclopropane), 1 374, 1 180 (methanesulfonate). For $C_{28}H_{48}O_3S$ (464·8) calculated: 72·36% C, 10·41% H, 6·90% S; found: 72·53% C, 10·37% H, 6·77% S.

3α,5-Cyclo-5α-cholestan-7β-ol Acetate (*VII*)

A) From 3α,5-*cyclo*-5α-*cholestan*-7β-*ol* (V). Acetic anhydride (0·6 ml) was added to a solution of alcohol *V* (60 mg) in pyridine (1 ml). After standing at room temperature for 20 h, the mixture was poured into water, the product was taken up in ether and worked up in the usual manner, affording 65 mg of noncrystalline acetate *VII*, $[\alpha]_D^{20}$ +74° (*c* 0·8). ^{1}H NMR spectrum: −0·08 to 0·13 m, 1 H and 0·26–0·42 m, 1 H (two cyclopropane protons); 0·70 s, 3 H (3 × H-18); 0·86 d, 6 H (3 × H-26 and 3 × H-27, J = 6); 0·93 s, 3 H (3 × H-19); 1·98 s, 3 H (CH_3COO); 4·58 m, 1 H (H-7α, $W_{1/2}$ = 26). IR spectrum: 3 060, 3 025 (cyclopropane), 1 736, 1 251, 1 031 (acetate). For $C_{29}H_{48}O_2$ (428·7) calculated: 81·25% C, 11·29% H; found: 81·10% C, 11·11% H.

B) From 3α,5-*cyclo*-5α-*cholestan*-7β-*ol methanesulfonate* (VI). Preparative TLC zones, containing the less polar product, in the preparation of olefin *VIII* (Procedure *D*) afforded 36 mg of acetate *VII*, $[\alpha]_D^{20}$ +76° (*c* 1·1). Mass spectrum (*m*/*z*): 428 (M^+), 368 (M − CH_3COOH; base peak).

3α,5-Cyclo-5α-cholest-7-ene (*VIII*)

A) From 3α,5-*cyclo*-5α-*cholestan*-α-*ol* (II). Methanesulfonyl chloride (1 ml) was added to a solution of alcohol *II* (1 g) in pyridine (5 ml). After standing at room temperature overnight, the reaction mixture was poured into water, the product was extracted with ether and worked up as usual to give a mixture (1·1 g) of compounds *III* and *VIII* which were separated by TLC in light petroleum–ether (9 : 1). Zones, containing the lipophilic product, afforded 170 mg of material which was crystallized from ethanol to give 112 mg of olefin *VIII*, m.p. 83–84°C, $[\alpha]_D^{20}$ +82° (*c* 0·7) in accord with the published[4] values. Mass spectrum (*m*/*z*): 368 (M^+, base peak), 353 (M − CH_3). IR spectrum (CS_2): 3 055 (cyclopropane), 3 020 and 1 673 (trisubstituted double bond). ^{1}H NMR spectrum: −0·12 to 0·21 m, 1 H and 0·29–0·48 m, 1 H (two cyclopropane protons); 0·86 d, 6 H (3 × H-26 and 3 × H-27, J = 6); 0·90 d, 3 H (3 × H-21, J = 6); 0·91 s, 6 H (3 × H-18 and 3 × H-19); 5·16 m, 1 H (H-7, $W_{1/2}$ = 9).

B) By acetolysis of 3α,7-*cyclo*-5α-*cholestan*-7α-*ol methanesulfonate* (III). Sodium acetate (400 mg) and methanesulfonate *III* (363 mg) were dissolved in a mixture of acetic acid (15 ml) and acetic anhydride (1·5 ml). After reflux for 4 h and standing overnight, the reaction mixture was poured into water and the product was taken up in ether. The ethereal layer was washed with water, 10% potassium hydrogen carbonate solution and water, dried and taken down. The residue (285 mg), which contained a mixture of compounds *VIII* and *IX*, was chromatographed on a column of silica gel (100 g) in light petroleum–ether (first 99 : 1, then 19 : 1). Fractions, containing the lipophilic product, afforded 196 mg of material which was crystallized from ethanol to give 171 mg of olefin *VIII*, m.p. 82–84°C, $[\alpha]_D^{20}$ +78° (*c* 1·1).

C) By hydrogenolysis of methanesulfonyloxy derivative III *with zinc.* Chromatographic fractions in the preparation of compound *XIV* (Procedure *A*), that contained medium lipophilic product, furnished 21 mg of olefin *VIII*, m.p. 80–84°C, $[\alpha]_D^{20}$ +81° (*c* 1·1).

D) By acetolysis of 3α,5-*cyclo*-5α-*cholestan*-7β-*ol methanesulfonate* (VI). A mixture of methanesulfonate *VI* (371 mg), sodium acetate (371 mg), acetic acid (15 ml) and acetic anhydride (1·5 ml) was refluxed under nitrogen for 4 h. After pouring into water, the reaction mixture was worked up analogously as described under *B*). The residue (270 mg), consisting (TLC) of 3 compounds (*VII*, *VIII* and *IX*) was subjected to preparative TLC on 8 plates, elution with light petroleum–ether (9 : 1). Fractions, containing lipophilic product, gave 36 mg of olefin *VIII*, m.p. 82–84°C, $[\alpha]_D^{20}$ +80° (*c* 0·4).

5-Cholesten-3β-ol Acetate (*IX*)

A) By acetolysis of 3α,5-*cyclo*-5α-*cholestan*-7α-*ol methanesulfonate* (III). Further chromatographic fractions in the preparation of olefin *VIII* (Procedure B) afforded 41 mg of polar crystalline material which was crystallized from methanol to give 28 mg of the title compound, m.p. 112–115°C, $[\alpha]_D^{20}$ −42° (*c* 1·1) in accord with ref.[5]. IR spectrum: 3 035, 1 652 (C=C), 1 737, 1 249, 1 037 (acetate). ^{1}H NMR spectrum: 0·68 s, 3 H (3 × H-18); 0·86 d, 6 H (H-26 and H-27, J = 6); 0·92 d, 3 H (H-21, J = 6); 1·03 s, 3 H (3 × H-19); 2·18–2·42 m, 1 H (H-4); 4·64 m, 1 H (H-3α, $W_{1/2}$ = 33); 5·40 m, 1 H (H-6, $W_{1/2}$ = 8).

B) By acetolysis of 3α,5-*cyclo*-5α-*cholestan*-7β-*ol methanesulfonate* (VI). Work-up of TLC zones, containing the most polar product, in the preparation of acetate *VII* (Procedure *B*) afforded 121 mg of 5-cholesten-3β-ol acetate (*IX*), m.p. 110–114°C, $[\alpha]_D^{20}$ −41° (*c* 1·1.).

3α,5-Cyclo-5α-cholestane (*XIV*)

A) From 3α,5-*cyclo*-5α-*cholestan*-7α-*ol methanesulfonate* (III) *by reaction with zinc.* Sodium iodide (0·2 g) and zinc powder (0·2 g) were added to a solution of methanesulfonate *III* (100 mg) in 1,2-dimethoxyethane (6 ml) and the mixture was refluxed under nitrogen for 40 h. The zinc was filtered off, the filtrate was poured into water and the product was extracted with ether. The ethereal layer was washed with 10% sodium thiosulfate solution and water, dried and taken down. The residue (79 mg), which consisted (TLC) of three products (*VIII*, *XIV* and *XV*), was separated by preparative TLC (6 plates) in light petroleum. Zones, containing the most lipophilic product, were worked up and the residue (15 mg) was crystallized from ethanol to give 11 mg of compound *XIV*, m.p. 78–79°C, $[\alpha]_D^{20}$ +80° (*c* 1·2), in accord with the reported[6] values. Mass spectrum (*m*/*z*): 370 (M^+), 355 ($M - CH_3$). ^{1}H NMR spectrum: −0·11 to 0·07 m, 1 H and 0·26–0·42 m, 1 H (two cyclopropane protons); 0·69 s, 3 H (3 × H-18); 0·87 d, 6 H (3 × H-26 and 3 × H-27, J = 6); 0·90 s, 3 H (3 × H-19); 0·91 d, 3 H (3 × H-21, J = 6). IR spectrum (CS_2): 3 055, 3 015 (cyclopropane).

B) From 3α,5-cyclo-5α-cholestan-7α-ol methanesulfonate (III) *by reaction with lithium aluminium hydride.* Lithium aluminium hydride (2·06 g) was added in small portions to a solution of compound *III* (1·03 g) in tetrahydrofuran (100 ml). After refluxing under nitrogen for 4 h, the mixture was cooled and the excess hydride was decomposed with ethyl acetate and methanol. The mixture was poured into water, the product was extracted with ether and processed in the usual manner. The obtained mixture (0·9 g) of *II* and *XIV* was chromatographed on a column of silica gel in light petroleum to give 140 mg of an oily material which was purified by preparative TLC in light petroleum. Yield 108 mg of compound *XIV*, m.p. 76–78°C, $[\alpha]_D^{20}$ +76° (*c* 1·1).

C) From 3α,5-cyclo-5α-cholestan-7β-ol methanesulfonate (VI) *by treatment with zinc.* Compound *VI* (319 mg) was hydrogenolyzed as described in procedure *A)* and the reaction mixture was worked up analogously. The obtained material (240 mg) contained (TLC), in addition to *XIV*, also traces of compounds of the same R_F as compounds *VIII* and *XV*. Purification on a column of silica gel (50 g; elution with light petroleum) afforded 211 mg of compound *XIV*, m.p. 75–77°C, $[\alpha]_D^{20}$ +79·5° (*c* 1·1).

D) From 3α,5-cyclo-5α-cholestan-7β-ol methanesulfonate (VI) *by treatment with lithium aluminium hydride.* Lithium aluminium hydride (0·6 g) was added to a solution of compound *VI* (300 mg) in anhydrous tetrahydrofuran (20 ml). After standing at room temperature for 100 min, the excess hydride was decomposed with ethyl acetate and methanol. The reaction mixture was poured into water and the product was extracted with ether and worked up in the usual manner. The obtained residue (240 mg; a mixture of *XIV* and *V*) was subjected to preparative TLC (10 plates) in light petroleum. Zones, containing lipophilic product, afforded 84 mg of material which was crystallized from ethanol to give 49 mg of compound *XIV*, identical in all respects with the product obtained by procedure *A)*; m.p. 78–79°C, $[\alpha]_D^{20}$ +80° (*c* 1·1).

3α,5-Cyclo-5α-cholest-6-ene (*XV*)

Preparative TLC fractions containing the least lipophilic compound in the preparation of compound *VIII* (Procedure *C*) afforded 38 mg of material which was crystallized from ethanol to afford 26 mg of olefin *XV*, m.p. 75–77°C, $[\alpha]_D^{20}$ −41° (*c* 1·5), in accord with the published[7] data. ^{1}H NMR spectrum: −0·34 to 0·51 m, 1 H (cyclopropane proton); 0·72 s, 3 H (3 × H-26 and 3 × H-27, J = 6); 0·91 s, 3 H (3 × H-19); 0·93 d, 3 H (3 × H-21, J = 6); 5·17 dd, 1 H (J = 3, J' = 10) and 5·52 dd, 1 H (J = 2, J' = 10) (6-H and 7-H). IR spectrum (CS_2): 3 055, 3 025 (C=C and cyclopropane), 1 640, 1 650 sh, 737 (C=C).

Elemental analyses were carried out in the Analytical Laboratory of this Institute by Mrs E. Sýkorová, Mrs E. Šípová and Mr V. Štěrba (Dr V. Pechanec, Head). The author is indebted to Dr J. Smolíková for interpretation of the IR *spectra measured by Mrs K. Matoušková. Mass spectra were measured by Mrs P. Loudová and Dr J. Kohoutová,* ^{1}H NMR *spectra by Mrs J. Jelínková and Mrs M. Snopková.*

REFERENCES

1. Kohout L., Sethi V. K., Zajíček J., Kasal A.: Collect. Czech. Chem. Commun. *51*, 436 (1986).
2. Kohout L.: Collect. Czech. Chem. Commun. *46*, 1828 (1981).
3. Kohout L., Fajkoš J.: Collect. Czech. Chem. Commun. *38*, 913 (1973).
4. Karrer P., Asmis H.: Helv. Chim. Acta *35*, 1926 (1952).
5. Bergmann E. D., Rabinowitz M., Levinson Z. H.: J. Am. Chem. Soc. *81*, 1239 (1959).
6. Prout F. S., Riegel B.: Helv. Chim. Acta *74*, 3190 (1952).
7. Riegel B., Hager G. P., Zenitz B. L.: J. Am. Chem. Soc. *68*, 2562 (1946).

Translated by M. Tichý.