Vitamin D relatives. Part I. B-thiophene-des-A-cholestanes. Solvolytic reactions of some derivatives of 2,2-disubstituted cyclohexane-1,4-diol and 4-hydroxycyclohexan-1-one

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Received December 6, 1985

JACEK W. MORZYCKI. Can. J. Chem. **64**, 1536 (1986).

Some derivatives of des-A-cholestane with a thiophene ring B have been prepared from triketone **2**. The reactions of tosylates of C-10 alcohols (**7***b*, **9***b*, and **8***c*) leading to A-ring ethers (**10** and **11**) and olefin **5**, respectively, have been studied. The solvolysis of tosylate **4***c* and the Bamford–Stevens reactions of *p*-tosylhydrazones **3***c* and **13***b* are also discussed.

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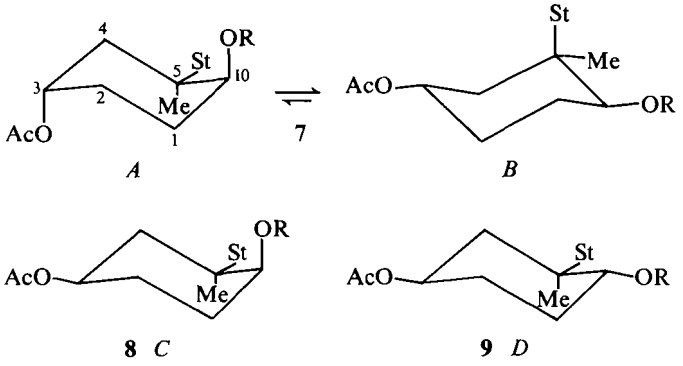
Utilisant la tricétone **2** comme produit de départ, on a préparé quelques dérivés du des-A-cholestane comportant un thiophène comme cycle B. On a étudié les réactions des tosylates des alcools en C-10 (**7***b*, **9***b* et **8***c*) qui conduisent respectivement aux éthers du cycle A (**10** et **11**) et à l'oléfine **5**. On discute aussi des réactions de solvolyse du tosylate **4***c* et des réactions de Bamford–Stevens des *p*-tosylhydrazones **3***c* and **13***b*.

[Traduit par la revue]

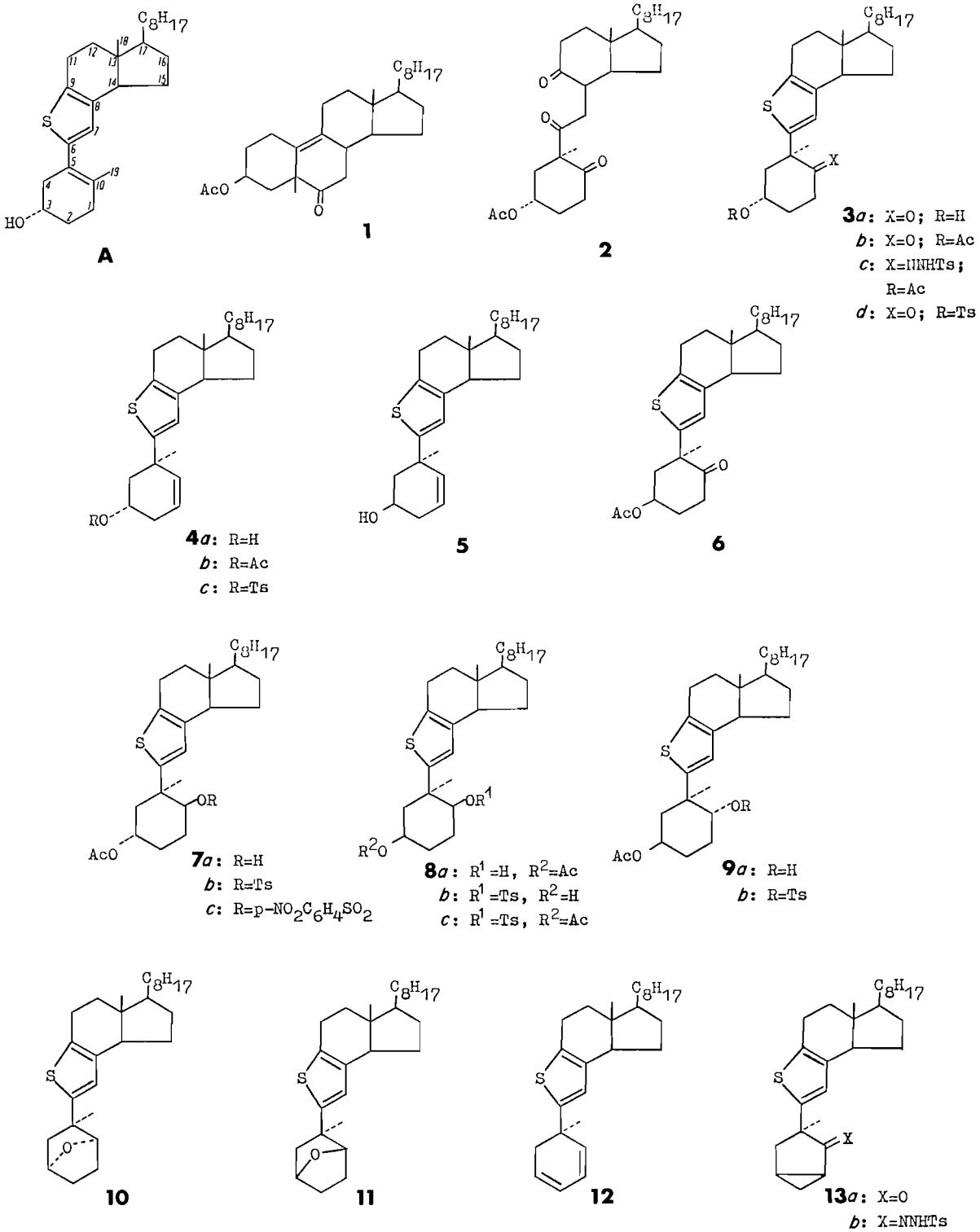
In the course of our studies on the synthesis of vitamin D relatives (1, 2) we have drawn attention to 6,9-epithio-tachysterol **A** as a possible intermediate. The allylic oxidation of this compound, followed by desulfurization, as well as photochemical and thermal isomerization (3) could afford an important, active metabolite of vitamin D_3, i.e. 1α-OH-D_3 (4). In an attempted synthesis of 6,9-epithio-tachysterol **A**, the starting ketone **1** (5) with the double bond C(9)—C(10) was subjected to ozonolysis. The resulting triketone **2** contained a 1,4-dicarbonyl system that reacted with phosphorus pentasulfide to give the thiophene derivative **3***b* (6) in good yield. In the next step the problem of the 19-methyl group migration from the 5β position to its former (in cholesterol) 10β position arose. It was expected that generation of a carbonium ion at C-10 should provide a driving force for the reaction. We assumed that the secondary carbonium ion adjacent to the quaternary carbon C-5 is likely to rearrange, to give a more stable tertiary carbonium ion by migration of a substituent (methyl, thienyl) or ring bond.

The carbon atom C-10 exists in compound **3***b* in the form of a carbonyl group and one of the best ways to the desired carbonium ion seemed to be the decomposition (7*a*) of 10-toluene-*p*-sulfonylhydrazone **3***d* under basic conditions (Bamford–Stevens reaction). The reaction afforded the unrearranged $\Delta^{1(10)}$ olefin **4***a* as the major product. The failure of this reaction prompted us to study the solvolytic reactions (7*b*) of *p*-toluenesulfonates of the C-10 alcohols. The $NaBH_4$ reduction of ketone **3***b* yielded a single epimer of alcohol **7***a*. As expected (attack of hydride from the less hindered side of the molecule), the compound obtained had the 10α-OH configuration. Proton nmr showed the equatorial orientation of both hydroxyl and acetoxyl groups (the broad signals of axial 10β ($w/2$ = 15 Hz) and 3α ($w/2$ = 20 Hz) protons at δ = 3.66 and 5.13, respectively) in the dominating conformation *B*. The alternative chair conformation *A* with the *anti*-coplanar arrangement of 10α-OH and 5β-CH_3 is less stable due to 1,3-diaxial interaction of 3β-acetoxyl and methyl groups. The reaction of 10α-tosylate **7***b* with KOH/diethylene glycol/diglyme (diglyme: diethylene glycol dimethyl ether) at 120°C afforded ether **10** in good yield. The product was apparently formed by an intramolecular attack of the 3β-alkoxyl ion from the back side on carbon C-10 in the boat conformation, which becomes more significant at higher temperature. This S_N2 type reaction unequivocally confirmed the *trans* relationship of 3β-acetate to the leaving group in the starting material **7***b*. Unfortunately the formation of the oxygen bridge precluded the development of a carbonium ion at C-10 and, at the same time, the retropinacolic rearrangement. To avoid this complication and to increase the contribution of the conformation with an axial hydroxyl (or tosyloxyl) group, we decided to study the solvolysis of compound **8***c* with the inverted configuration of acetate at C-3. Acetylation with inversion (8) of hydroxy-ketone **3***a* gave **6**. The $NaBH_4$ reduction of ketone **6** resulted in the formation of two products in the ratio 4:3. The less polar, major product appeared to be the 10α alcohol **8***a*. The ^1H nmr spectra confirmed the domination of the expected conformation *C*, with the axial substituent at C-10 and the equatorial 3α-acetate, either in the case of free alcohol **8***a* or its tosylate **8***c* (δ 5.08 (m, $w/2$ = 24 Hz, 3β-H) and 4.57 ($w/2$ = 6 Hz, 10β-H)).



The second, more polar product was identified as the 10β alcohol **9***a*. The formation of significant amounts of epimeric alcohol **9***a* can be explained by taking into consideration its relative stability. In the preferred conformation *D*, either alcohol **9***a* or its tosylate **9***b* (δ 4.96 (m, $w/2$ = 22 Hz, 3β-H), 4.75 (m, $w/2$ = 18 Hz, 10α-H)) contained three equatorial substitutents, and only the small methyl group that occupied the axial position was involved in the 1,2-ae interaction with a 10β substituent.

The solvolysis of 10α-tosylate **8***c* was carried out under the same conditions as described in the case of compound **7***b*. Although the preferred conformation *C* seemed to be the most favourable for the methyl group migration, the reaction afforded $\Delta^{1(10)}$ olefin **5** and no rearranged products were detected. The



SCHEME 1

minor product of the reaction appeared to be hydroxy-tosylate **8***b* (the elimination of TsOH must be slower than the intramolecular substitution observed in the case of **7***b*). The similar reaction of the 10β-tosylate **9***b* resulted in the formation of α-ether **11** as the only isolable product. This intramolecular displacement proceeded in the same way as described above for compound **7***b*. In this case a nucleophilic attack took place from the opposite, α, side of the molecule as required by the structure of the starting material.

Since we failed to obtain the rearranged products by solvolytic methods from tosylates of the C-10 alcohols, we tried some other reactions that could afford at least partial positive charge at C-10. Such a reaction was the solvolysis of tosylate **4***c*, which should proceed with participation of π-electrons of the double bond. A nonclassical carbocation with a considerable charge at C-10 could be a suitable intermediate for rearrangement. The compound **4***c* was obtained by tosylation of homoallylic alcohol **4***a*, the product of the decomposition of *p*-tosylhydrazone **3***c*

already described. However, the reaction, carried out in the same manner as described previously, yielded only the product of a simple elimination of *p*-TsOH, diene **12**. Another attempt was the Bamford–Stevens reaction of *p*-tosylhydrazone **13***b*. The α-cyclopropyl ketone **13***a* was easily obtained from oxo-tosylate **3***d* by the reaction with sodium isopropoxide in almost quantitative yield. Unfortunately the decomposition of **13***b* under basic conditions led to a complex mixture of products, which were not analysed.

Eventually, we brought about the migration of the 19-methyl group by solvolysis of *p*-nitrobenzenesulfonate **7***c* in refluxing acetic acid in the presence of sodium acetate. Under these conditions, mainly the products of methyl migration were formed, in addition to a small amount of unrearranged olefin **4***b*. However, 6,9-epithio-tachysteryl acetate (λ_{max} 294 nm, δ 1.88 (br s, 19-H)), obtained in low yield, was accompanied by a number of other products (e.g. the $\Delta^{4(5)}$ isomer, nonpolar products of rearrangement with concomitant 3β-acetate elimination). The process requires further studies, which are under way.

Experimental

The melting points were determined on a Boetius micro melting point apparatus and are uncorrected. Optical rotations were measured on a Perkin–Elmer 241 polarimeter in chloroform solutions at $c = 1.0$ unless otherwise stated. The ir spectra were recorded on UR-20 and Unicam SP 1100 spectrophotometers. The ^{1}H nmr spectra were taken at 100 mHz (JEOL INM-4H-100 and Brüker instruments) in $CDCl_3$ solutions with TMS as an internal standard. Column chromatography was performed on silica gel (Kieselgel 60, 70–230 mesh, Merck). Thin-layer chromatograms were developed on aluminium tlc sheets precoated with silica gel F_{254} and visualized with 50% sulfuric acid after heating. All solvents were dried and freshly distilled prior to use. The starting ketone **1** was prepared according to the procedure described in ref. 5.

Triketone 2

A solution of β,γ-unsaturated ketone **1** (2.5 g) in hexane (100 mL) was cooled to −70°C in a Dry Ice – acetone bath and then treated with ozone. An excess of ozone was removed by passing a stream of oxygen, the reaction mixture was allowed to warm up to room temperature, and hexane was evaporated under reduced pressure. The residue was dissolved in acetic acid (30 mL) and stirred with zinc dust (2.5 g) for 45 min. The reaction mixture was diluted with ether (250 mL) and all inorganic material was filtered off. The filtrate was washed with water, sodium bicarbonate solution, again with water, and dried over anhydrous sodium sulfate. The solvent was removed and the crude product was purified on a silica gel column. Triketone **2** (1.9 g) was eluted with benzene–ether (9:1); $[\alpha]_D^{27}$ −68.2°; ν_{max} (neat): 1732, 1713, and 1698 cm^{-1}; δ: 5.42 (m, 1H, 3α-H), 2.08 (s, 3H, CH_3COO—), 1.38 (s, 5β-CH_3), 1.03 (s, 13β-CH_3). *Anal.* calcd. for $C_{29}H_{46}O_5$: C 73.4, H 9.8; found: C 73.5, H 9.7.

β-Oxo-thiophenes 3

To a stirred solution of triketone **2** (500 mg) in anhydrous THF (50 mL) were added phosphorus pentasulfide P_4S_{10} (1 g) and potassium hydrogen carbonate (1 g) and the reaction mixture was refluxed for 1 h. Most of the solvent was distilled off and the residue was dissolved in tetrachloromethane and water. The organic solution was washed with water, dried, and evaporated. Silica gel column chromatography of the crude product afforded compound **3***b* in a pure form (310 mg; 62%) eluted with benzene–ether (1%). At the end of elution some fractions containing **3***b* were contaminated by a slightly more polar furan analog (δ: 6.10 (s, 7-H)). Therefore it is recommended to leave the crude product for a few days in CCl_4 solution before chromatography to get rid of the unstable furan derivative. Compound **3***b*: $[\alpha]_D^{27}$ −72°; ν_{max} ($CHCl_3$): 1730, 1716, and 1261 cm^{-1}; λ_{max} (EtOH): 240 nm (ε 4950); δ: 6.53 (s, 1H, 7-H), 5.43 (m, 1H, 3α-H), 2.08 (s, 3H, CH_3COO—), 1.37 (s, 5β-CH_3), 0.61 (s, 13β-CH_3). *Anal.* calcd. for $C_{29}H_{44}O_3S$: C 73.7, H 9.4; found: C 73.6, H 9.4.

The hydrolysis of **3***b* was carried out in the following way. Compound **3***b* (140 mg) was dissolved in ethanol (20 mL) and a solution of potassium hydroxide (200 mg) in water (1 mL) was added dropwise. The reaction mixture was kept at 40°C for 1 h. The usual work-up afforded hydroxy-ketone **3***a* as an amorphous solid, $[\alpha]_D^{24}$ −76°; ν_{max} (KBr): 3430 and 1721 cm^{-1}; δ: 6.38 (s, 1H, 7-H), 4.30 (m, 1H, 3α-H), 3.41 (bs, 1H, —OH), 1.36 (s, 5β-CH_3), 0.60 (s, 13β-CH_3).

*3β-Hydroxy-olefin 4*a

Compound **3***b* (150 mg) and toluene-4-sulfonic acid hydrazide (250 mg) were dissolved in diglyme (2 mL) – diethylene glycol (5 mL) mixture, and acetic acid (0.5 mL) was added. The reaction mixture was stirred at 70°C for 4 h; tlc control showed the disappearance of all the starting material. A solution of *p*-tosylhydrazone **3***c* obtained in such a way was treated with KOH (2.5 g) and the temperature was increased to 140°C. The reaction was maintained at this temperature until evolution of N_2 stopped (about 30 min). After cooling, the reaction mixture was poured into 3% sulfuric acid and extracted with methylene chloride. The extract was dried over sodium sulfate and evaporated (the rest of the diglyme and glycol was removed under high vacuum) and the residue was chromatographed on a silica gel column. The product, olefin **4***a*, was eluted with benzene–ether (3%). Yield 76 mg; $[\alpha]_D^{24}$ +114°; ν_{max} ($CHCl_3$): 3610 and 1034 cm^{-1}; δ: 6.37 (s, 1H, 7-H), 5.69 (almost s, 2H, 1-H and 10-H), 3.90 (m, 1H, 3α-H), 1.41 (s, 5β-CH_3), 0.61 (s, 13β-CH_3). *Anal.* calcd. for $C_{27}H_{42}OS$: C 78.2, H 10.2; found: C 78.4, H 10.1.

*3β,10α-Diol 3-monoacetate 7*a

A stirred solution of compound **3***b* (200 mg) in benzene (15 mL) – methanol (15 mL) was treated with sodium borohydride (50 mg). After 30 min at room temperature the solvents were removed, chloroform and 5% sulfuric acid were added, and the chloroform layer was separated, washed with water, and dried over sodium sulfate. The evaporation of the solvent afforded essentially pure 10α-alcohol **7***a* in almost quantitative yield; mp 170–171°C (from hexane); $[\alpha]_D^{26}$ +32.5° (*c* 0.9); ν_{max} (KBr): 3474, 1718, and 1272 cm^{-1}; λ_{max} (EtOH): 241 nm (ε 6900); δ: 6.61 (s, 1H, 7-H), 5.13 (m, $w/2 = 20$ Hz, 1H, 3α-H), 3.66 (m, $w/2 = 15$ Hz, 1H, 10β-H), 2.05 (s, 3H, CH_3COO—), 1.83 (s, —OH), 1.42 (s, 5β-CH_3), 0.62 (s, 13β-CH_3). *Anal.* calcd. for $C_{29}H_{46}O_3S$: C 73.4, H 9.8; found: C 73.5, H 9.6.

Compound **7***a* (70 mg) and *p*-TsCl (170 mg) were dissolved in anhydrous pyridine (3 mL) and the solution was allowed to stand at room temperature for 24 h. The usual work-up gave tosylate **7***b*, which was used in the next experiment.

3β,10β-Ether 10

Tosylate **7***b* from the previous experiment was dissolved in diglyme (3 mL), potassium hydroxide (1.2 g) in diethylene glycol (3 mL) was added, and the vigorously stirred reaction mixture was heated at 120°C for 1 h. After cooling, the reaction mixture was poured into dilute hydrochloric acid and extracted with tetrachloromethane. The extract was washed with water, dried over sodium sulfate, and evaporated. The crude product **10** was filtered through a layer of silica gel in a benzene–ether (2%) solution. Yield 39 mg; $[\alpha]_D^{26}$ +18° (*c* 0.86); ν_{max} ($CHCl_3$): 1017 cm^{-1}; λ_{max} (EtOH): 241 nm (ε 7000); δ: 6.42 (s, 1H, 7-H), 4.64 and 4.23 (2 × m, 2 × 1H, —CH—O—CH—), 1.42 (s, 5β-CH_3), 0.62 (s, 13β-CH_3). *Anal.* calcd. for $C_{27}H_{42}OS$: C 78.2, H 10.2; found: C 78.5, H 10.2.

3α-Acetoxy-ketone 6

To a stirred solution of 3β-hydroxy-ketone **3***a* (300 mg) triphenylphosphine (250 mg), and acetic acid (100 mg) in anhydrous tetrahydrofuran (5 mL) was added diethyl azodicarboxylate (180 mg), and the reaction mixture was allowed to stand at room temperature for 24 h. The solvent was evaporated and the residue was chromatographed on a silica gel column. The steroidal product **6** was eluted with benzene–ether (5%). Yield 220 mg; $[\alpha]_D^{24}$ −6.0°; ν_{max} ($CHCl_3$): 1730 and 1705 cm^{-1}; δ: 6.37 (s, 1H, 7-H), 5.24 (m, 1H, 3β-H), 1.93 (s, 3H,

CH_3COO—), 1.49 (s, 5β-CH_3), 0.62 (s, 13β-CH_3). *Anal.* calcd. for $C_{29}H_{44}O_3S$: C 73.7, H 9.4; found: C 73.9, H 9.5.

3α,10α-Diol- and 3α,10β-diol-3-monoacetates **8**a *and* **9**a

A solution of compound **6** (200 mg) in benzene–methanol (1:1; 30 mL) was treated with $NaBH_4$ (50 mg) at room temperature for 1 h. The usual work-up of the reaction mixture, followed by the chromatographic separation of products on a silica gel column afforded 10α-alcohol **8***a* (108 mg) and 10β-alcohol **9***a* (82 mg); both products were eluted with benzene–ether (6%).

Compound **8***a*: $[\alpha]_D^{24}$ +65.0°; ν_{max} (neat): 3620, 1732, and 1248 cm^{-1}; δ: 6.53 (s, 1H, 7-H), 5.02 (m, 1H, 3β-H), 3.68 (m, 1H, 10β-H), 2.06 (s, 3H, CH_3COO—), 1.78 (s, —OH), 1.39 (s, 5β-CH_3), 0.61 (s, 13β-CH_3). *Anal.* calcd. for $C_{29}H_{46}O_3S$: C 73.4, H 9.8; found: C 73.7, H 9.8.

Compound **9***a*: $[\alpha]_D^{24}$ +63.8°; ν_{max} (neat): 3525, 1739, and 1248 cm^{-1}; δ: 6.56 (s, 1H, 7-H), 5.00 (m, 1H, 3β-H), 3.77 (m, 1H, 10α-H), 2.00 (s, 3H, CH_3COO—), 1.38 (s, 5β-CH_3), 0.62 (s, 13β-CH_3). *Anal.* calcd. for $C_{29}H_{46}O_3S$: C 73.4, H 9.8; found: C 73.6, H 9.7.

Both alcohols were converted into the corresponding tosylates **8***c* or **9***b* by dissolving the starting material (70 mg) in anhydrous pyridine (3 mL) together with *p*-tosyl chloride (300 mg). The reactions were allowed to stand at 30°C for 1 week. The standard work-up followed by chromatographic purification (tosylates were eluted with benzene–ether (2%) in both cases) afforded compounds **8***c* or **9***b* in almost quantitative yields.

8*c*: δ: 7.26 (AA′BB′, J = 8.4 Hz, 4H, arom. H), 6.38 (s, 1H, 7-H), 5.08 (m, $w/2$ = 24 Hz, 1H, 3β-H), 4.57 (m, $w/2$ = 6 Hz, 1H, 10β-H), 2.40 (s, 3H, Ar-CH_3), 2.03 (s, 3H, CH_3COO—), 1.35 (s, 5β-CH_3), 0.58 (s, 13β-CH_3).

9*b*: δ: 7.27 (AA′BB′, J = 8.2 Hz, 4H, arom. H), 6.37 (s, 1H, 7-H), 4.96 (m, $w/2$ = 22 Hz, 1H, 3β-H), 4.75 (m, $w/2$ = 18 Hz, 1H, 10α-H), 2.40 (s, 3H, Ar-CH_3), 1.97 (s, 3H, CH_3COO—), 1.38 (s, 5β-CH_3), 0.58 (s, 13β-CH_3).

3α,10α-Ether **11**

To a solution of tosylate **9***b* (67 mg) in diglyme (3 mL) was added potassium hydroxide (1.2 g) in diethylene glycol (3 mL). The reaction mixture was heated at 120°C and stirred for 1 h. The reaction was quenched in cold water, acidified with hydrochloric acid, and extracted with tetrachloromethane. The extract was washed with water, dried (anhydrous Na_2SO_4), and evaporated. The crude produce was purified on a silica gel column. 3α,10α-Ether **11** (37 mg) was eluted with benzene–ether (1%); $[\alpha]_D^{24}$ +33.5°; ν_{max} ($CHCl_3$): 995 cm^{-1}; λ_{max} (EtOH): 240 nm (ε 6200); δ: 6.49 (s, 1H, 7-H), 4.65 and 4.36 (2 × m, 2 × 1H, —CH—O—CH—), 1.42 (s, 5β-CH_3), 0.54 (s, 13β-CH_3). *Anal.* calcd. for $C_{27}H_{42}OS$: C 78.2, H 10.2; found: C 78.5, H 10.1.

3α-Hydroxy-olefin **5**

The solvolysis of tosylate **8***c* (70 mg) was carried out in exactly the same manner as in the previous experiment. The reaction products were separated on a silica gel column. The elution with benzene–ether (4%) afforded 3α-hydroxy-olefin **5** (36 mg). With benzene–ether (7%), hydroxy-tosylate **8***b* (10 mg) was eluted.

Compound **5**: $[\alpha]_D^{24}$ + 61°; ν_{max} ($CHCl_3$): 3618 and 1038 cm^{-1}; δ: 6.47 (s, 1H, 7-H), 5.68 (m, 1H, 1-H), 4.08 (m, 1H, 3β-H), 1.45 (s, 5β-CH_3), 0.63 (s, 13β-CH_3). *Anal.* calcd. for $C_{27}H_{42}OS$: C 78.2, H 10.2; found: C 78.4, H 10.4.

Compound **8***b*: $[\alpha]_D^{24}$ +52°; ν_{max} ($CHCl_3$): 3606, 1178, and 901 cm^{-1}; δ: 7.27 (AA′BB′, J = 8.4 Hz, 4H, arom. H), 6.41 (s, 1H, 7-H), 4.54 (m, 1H, 10β-H), 3.98 (m, 1H, 3β-H), 2.41 (s, 3H, Ar-CH_3), 1.34 (s, 5β-CH_3), 0.59 (s, 13β-CH_3).

Diene **12**

3β-Hydroxy-olefin **4***a* (80 mg) and *p*-tosyl chloride (300 mg) were dissolved in anhydrous pyridine and allowed to stand for 16 h. Thin-layer chromatography showed complete conversion and the pyridine was then evaporated at room temperature. The residue was dissolved in diglyme (2 mL) and a solution of KOH (0.8 g) in diethylene glycol was added. The reaction mixture was vigorously stirred and heated at 110°C for 30 min. The reaction was quenched in cold water, acidified with HCl, and extracted with tetrachloromethane. The solvent was removed from the extract dried over sodium sulfate, and the crude product was purified by filtration through a layer of silica gel in a benzene – petroleum ether (1:4) solution. Yield of diene **12**, 56 mg; $[\alpha]_D^{25}$ +155°; ν_{max} ($CHCl_3$): 2965 and 1471 cm^{-1}; λ_{max} (EtOH): 244 (ε 12 000) and 256 (ε 11 600) nm; δ: 6.51 (s, 1H, 7-H), 5.86 (m, 4H, 1-H, 2-H, 3-H, and 10-H), 1.42 (s, 5β-CH_3), 0.64 (s, 13β-CH_3). *Anal.* calcd. for $C_{27}H_{40}S$: C 81.8, H 10.2; found: C 81.5, H 10.0.

α-Cyclopropylketone **13**a

A solution of compound **3***a* (140 mg) and *p*-tosyl chloride (500 mg) in anhydrous pyridine (5 mL) was allowed to stand at room temperature for 16 h. Pyridine was removed under high vacuum and a solution of sodium isopropoxide in isopropanol (prepared from 1 g of sodium and 80 mL of i-PrOH) was added. The suspension obtained was refluxed for 1 h. Then water was added and isopropanol was distilled off under reduced pressure. The steroidal product was extracted with benzene, and the extract was dried over sodium sulfate and evaporated. The crude product was purified on a silica gel column, and α-cyclopropylketone **13***a* (105 mg) was eluted with benzene; mp 69–70°C; $[\alpha]_D^{25}$ +19.8°; ν_{max} ($CHCl_3$): 1699 cm^{-1}; δ: 6.48 (s, 1H, 7-H), 1.42 (s, 5β-CH_3), 0.61 (s, 13β-CH_3). *Anal.* calcd. for $C_{27}H_{40}OS$: C 78.6, H 9.8; found: C 78.5, H 9.8.

The *p*-tosylhydrazone of α-cyclopropylketone **13***b* was obtained in a manner similar to that described earlier for compound **3***c* (the reaction was somewhat slower and required more acetic acid). Its decomposition (Bamford–Stevens reaction), however, resulted in the formation of a complex mixture of products, which was not studied further.

Acknowledgements

Sincere thanks are extended to Professor W. J. Rodewald for useful discussions. This investigation was supported by the Polish Academy of Sciences.

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