Preparation and Determination of Configuration of 3-Halogeno-3-methyl-5α-cholestane Epimers

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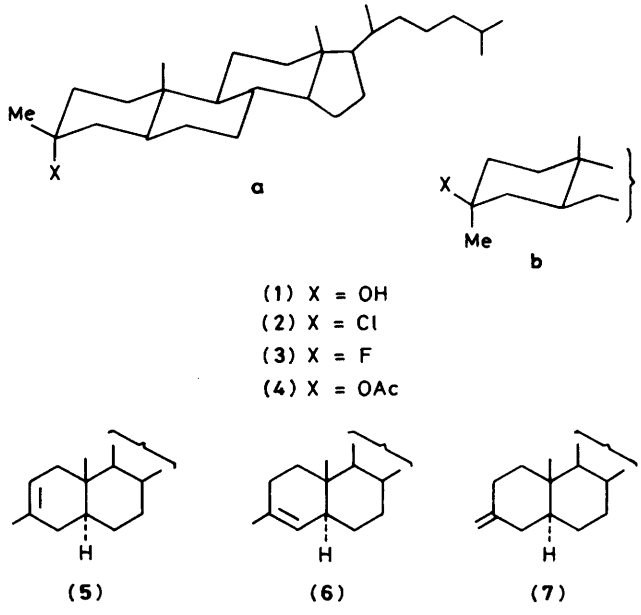
3α-Chloro-3β-methyl- and 3β-chloro-3α-methyl-5α-cholestane were prepared by reaction of hydrochloric acid with the two epimeric 3-hydroxy-3-methyl-5α-cholestanes. A better yield and cleaner conversion could be obtained with tetramethyl-1-chlorovinylamine as chlorinating agent. Reaction of the two 3-methyl-5α-cholestanols with triphenylphosphine–carbon tetrachloride or phosphorus trichloride oxide–pyridine gave mixtures of 3-methyl-5α-cholest-2-ene, 3-methyl-5α-cholest-3-ene, and 3-methylene-5α-cholestane. The two epimeric 3-fluoro-3-methyl-5α-cholestanes were obtained by treatment of the two 3-methyl-5α-cholestan-3-ols with (diethylamino)sulphur trifluoride. The configuration of the 3-halogeno-3-methyl-5α-cholestanes was determined from their ^{13}C n.m.r. spectra. The availability of both 3-halogeno-3-methyl-5α-cholestane epimers allowed an unambiguous interpretation of the i.r. spectra in the 800—400 cm^{-1} region.

For the study of the transformation of tertiary hydroxy compounds into halogeno derivatives, we selected the two epimeric 3-methyl-3-hydroxy-5α-cholestanes (**1a**) and (**1b**). These compounds had already been examined by Barton *et al.*,[1] who obtained the same 3-chloro-3-methyl-5α-cholestane by reaction of both alcohols with hydrochloric acid.

In contrast, reaction with Ph_3P–CCl_4[2] gave a product which had a single spot on t.l.c. and which was shown to be an anhydro derivative by mass spectroscopy. However, from the presence of three vinylic resonances (centred at δ_H 5.24, 4.96, and 4.52) in the ^1H n.m.r. spectrum, it was obvious that we had obtained a mixture of alkenes (**5**), (**6**), and (**7**). Since h.p.l.c. analysis on silica gel could not differentiate the three anhydro isomers in the mixture, and since gas-liquid chromatography on different stationary phases such as OV1, OV17, or QF1 did not separate the internal alkenes (**5**) and (**6**), only n.m.r. spectroscopy could be used for an estimation of the relative amounts of the different isomers. The pure anhydro derivatives (**5**) and (**7**) were prepared as described before,[1] respectively by dehydration of alcohol (**1a**) or (**1b**) with perchloric acid–acetic acid and by Wittig reaction on 5α-cholestan-3-one. By comparison with these reference substances, we could determine by n.m.r. spectroscopy that alcohol (**1a**) gave a mixture of alkenes (**5**), (**6**), and (**7**) in the proportions 70:24:6; alcohol (**1b**) gave the same three products in the proportions 22:8:70.

By reaction of alcohols (**1a**) and (**1b**) with phosphorus trichloride oxide in pyridine, we obtained mixtures of similar composition as with Ph_3P–CCl_4. It should be noted that Barton *et al.*[1] mention that reaction of compound (**1a**) with $POCl_3$ gave alkene (**5**) in high yield, and that alcohol (**1b**) yielded a mixture containing mainly alkene (**7**). Thus, the main conclusion of that study is still valid.

We repeated the reaction of alcohols (**1a**) and (**1b**) with hydrochloric acid in dioxane,[1] and we confirmed that both epimers gave the same 3-chloro-3-methyl-5α-cholestane. To that compound the 3β-chloro-3α-methyl configuration has been assigned.[1] A 3α-chloro-3β-methyl configuration (**2a**) is more likely, in analogy with the data published for the bromo compounds.[3] T.l.c. of the mother liquors of this synthesis gave an indication of the presence of the epimer (**2b**), which could be isolated in poor yield. Because of the difficulty in purification of compound (**2b**), we examined the use of chloro enamine reagents. We found that reaction of alcohol (**1a**) with tetramethyl-1-chlorovinylamine [*NN*-dimethyl(1-chloro-2-methylprop-1-enyl)amine] [$Me_2C{=}C(Cl)NMe_2$] in dichloromethane in the presence of zinc chloride[4] gave chloride (**2b**) in 60% yield. A certain amount of anhydro derivatives (**5**) and (**7**) (ratio 4:1) was also formed. Other Friedel–Crafts-type catalysts gave a similar result or lower yields. Treatment of alcohol (**1b**) with the same reagent and with titanium chloride as catalyst yielded chloride (**2a**) in almost quantitative yield.



In contrast with the reaction of the tertiary alcohols with hydrochloric acid, where an intermediate carbonium ion gave mainly the more stable 3α-chloro epimers, the reaction with this enamine reagent proceeds mainly through an S_N2 mechanism with inversion of configuration.

We also observed that the Vilsmeier–Haack reagent $(Me_2N{=}CHCl)^+Cl^-$, which also has been used to replace hydroxy groups by chlorine,[5] gives only anhydro compounds upon reaction with alcohol (**1a**) or (**1b**).

Reaction of alcohol (**1a**) with (diethylamino)sulphur trifluoride (DAST) in dichloromethane at low temperature gave mainly a mixture of alkenes (**5**), (**6**), and (**7**) in the proportions 80:15:5, together with some 14% of the 3β-fluoro compound

Table. ^{13}C Chemical shifts[a] and assignments[b] of 3-substituted 3-methyl-5α-cholestanes

Carbon	(1a)	(1b)	(4a)	*c*	(4b)	*d*	(2a)	(2b)	(3a)		(3b)	
1	34.0	36.6	34.0	(37.2)	35.6	(33.4)	34.6	36.8	33.9		36.6	($^3J_{CF}$ 11 Hz)
2	34.8	36.5	32.1	(27.9)	32.7	(26.5)	37.6	38.7	32.9	($^2J_{CF}$ 23 Hz)	33.8	($^2J_{CF}$ 22 Hz)
3	69.5	71.2	81.8	(73.5)	83.4	(69.8)	72.9	75.5	94.2	($^1J_{CF}$ 166 Hz)	100.7	($^1J_{CF}$ 166 Hz)
3-Me	31.5	26.6	26.2		22.6		34.3	27.9	27.8	($^2J_{CF}$ 22 Hz)	24.6	($^2J_{CF}$ 26 Hz)
4	41.8	43.4	39.1	(34.5)	39.2	(33.4)	44.1	45.4	39.8	($^2J_{CF}$ 23 Hz)	40.6	($^2J_{CF}$ 22 Hz)
5	41.0	44.3	41.0	(45.1)	43.3	(40.6)	41.7	44.4	40.7		44.5	($^3J_{CF}$ 10 Hz)
6	28.4	28.7	28.0	(29.1)	28.5	(28.7)	28.2	28.8	28.3		28.7	
7	31.9	32.0	31.8	(32.4)	31.9	(32.4)	31.9	31.9	31.9		32.0	
8	35.5	35.6	35.4	(36.0)	35.6	(36.0)	35.6	35.7	35.5		35.8	
9	54.2	54.6	54.2	(54.9)	54.2	(54.9)	54.0	54.3	54.0		54.5	
10	35.5	35.6	35.2	(35.9)	35.4	(36.1)	35.6	35.4	35.1		35.5	
11	20.9	21.2	21.0	(21.7)	21.0	(21.3)	21.0	21.1	21.0		21.3	
12	28.1	28.1	28.1	(28.5)	28.1	(28.7)	28.0	28.3	28.1		28.2	
13	42.5	42.6	42.5	(43.0)	42.5	(43.0)	42.7	42.6	42.6		42.7	
14	56.2	56.4	56.2	(57.0)	56.2	(57.1)	56.4	56.3	56.3		56.5	
15	24.1	24.1	24.1	(24.5)	24.1	(24.5)	24.2	24.1	24.1		24.2	
16	40.0	40.1	39.9	(40.5)	39.9	(40.6)	40.1	40.0	40.0		40.1	
17	56.5	56.6	56.4	(57.0)	56.3	(57.1)	56.5	56.4	56.5		56.6	
18	12.0	12.0	12.0	(12.3)	12.0	(12.3)	12.0	12.0	12.0		12.1	
19	11.1	11.8	11.5	(12.3)	11.8	(11.5)	11.9	11.8	11.1		11.9	
20	35.7	36.0	35.7	(36.2)	35.8	(36.3)	35.8	35.8	35.7		35.8	
21	18.6	18.6	18.6	(19.0)	18.5	(19.0)	18.7	18.6	18.6		18.7	
22	36.1	36.2	36.1	(36.7)	36.0	(36.7)	36.2	36.1	36.1		36.2	
23	23.8	23.8	23.7	(24.4)	23.7	(24.4)	23.9	23.8	23.8		23.9	
24	39.4	39.5	39.4	(39.9)	39.4	(40.0)	39.6	39.4	39.5		39.6	
25	27.8	27.9	27.8	(28.3)	27.8	(28.3)	28.0	28.1	27.9		28.0	
26	22.4	22.4	22.4	(22.7)	22.4	(22.8)	22.5	22.5	22.4		22.5	
27	22.6	22.6	22.7	(22.9)	22.6	(23.0)	22.7	22.7	22.6		22.7	
$COCH_3$			22.4	(20.9)	22.4	(21.0)						
C=O			170.3	(169.7)	170.2	(169.6)						

[a] In p.p.m. from Me_4Si. [b] Assignments for some close lying resonances may be interchanged. [c] Literature values[6] for 3α-acetoxy-5β-cholestane in parentheses. [d] Literature values[6] for 3β-acetoxy-5α-cholestane in parentheses.

(**3b**). Again, treatment of alcohol (**1b**) with DAST yielded the fluoride (**3a**) in almost quantitative yield. This result is very similar to that obtained with tetramethyl-1-chlorovinylamine.

Configurations of the different cholestane derivatives were readily assigned from their ^{13}C n.m.r. spectra by comparing, for each pair of epimers, the chemical shift of the 3-Me carbon. As can be seen in the Table, the signal of this carbon, which is easily identified by the SFORD technique, is shifted 3—6 p.p.m. upfield for all compounds having a 3α-oriented or axial 3-Me substituent (series **b**). Indeed, one of the characteristic features of ^{13}C n.m.r. spectroscopy in alicyclic compounds is the fact that an axially oriented substituent generally will resonate at higher field than an equatorial one. Thus when the two epimers are available the shift position of the 3-Me carbon seems to be an easily applied and valuable diagnostic criterion to distinguish 3α- from 3β-isomers.

Assignments of the carbon resonances given in the Table were straightforward. Introduction of a substituent in ring A of the steroid skeleton is expected to have no or only very little influence on the shifts of distant carbons, and thus the resonances for carbons of rings B, C, and D and of the side-chain were all assigned in accordance with literature data for 5α-cholestan-3β-ol,[6] and were confirmed as far as possible by SFORD spectra. Ring-A carbons (C-1—C-5) could be identified by comparison of spectra of related compounds and by application of known substituent parameters in cyclohexanes,[7] taking into account the fact that a possible breakdown of the additivity rule for geminal substituents may cause a less satisfying agreement with calculated shifts. Confirmation of our signal assignments for the two 3-methyl-5α-cholestan-3-ols was obtained from the acetylation shifts observed for the acetyl derivatives (**4a**) and (**4b**), and by comparison with published spectra[6] of 3α- and 3β-acetoxy-5α-cholestane. Compounds (**4a**) and (**4b**) were prepared in good yield by acetylation of the corresponding alcohols with acetic anhydride in the presence of dimethylaminopyridine (DMAP) and triethylamine in dichloromethane. The coherent chemical-shift changes for ring-A carbons add further evidence to the proposed configuration at C-3 of the cholestanes described in this report. Another valuable indication, at least for the configuration of the fluoro derivatives, is the occurrence of vicinal carbon–fluorine coupling ($^3J_{CF}$) which is known[8] to exhibit the same Karplus-type dependence on dihedral angle as all other vicinal couplings. In accord with this, we found in the β-isomer (**3b**) a $^3J_{CF}$ of *ca.* 10 Hz [F and C-1 or C-5 are anti-oriented (φ = 180°)] while in (**3a**) where the dihedral angle between F and C-1 or C-5 is *ca.* 60°, no vicinal coupling is observed. It should be noted that the previously determined[1] configuration of the two tertiary alcohols, which was assigned on the basis of i.r. spectra, corresponds with our results.

The i.r. data for the chloro derivatives show two absorption frequencies for each epimer in the region between 800 and 400 cm^{-1}, *e.g.* bands at 782 and 560 cm^{-1} for the axial chloro compound (**2a**) and at 790 and 690 cm^{-1} for the equatorial epimer (**2b**). As discussed in earlier i.r. studies,[9,10] this clearly indicates that the high-frequency band at about 785 cm^{-1} is not characteristic for (tertiary) C–halogen stretching. Instead, a weaker band at 558 cm^{-1} was considered[10] typical for an axial C–Cl band [we found 560 cm^{-1} for (**2a**)]. For the equatorial epimer (**2b**) which was not available at that time, Altona *et al.*[10] predicted a C–Cl stretching absorption near 650 cm^{-1}; we found experimentally a value of $\nu_{max.}$ 690 cm^{-1}. The i.r. data for the

fluoro derivatives show a C–F stretching absorption for the axial derivative (**3a**) at 892 cm^{-1}.

Experimental

M.p.s were measured using a Büchi apparatus and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer Model 580B spectrophotometer. ^{13}C N.m.r. spectra were obtained on a Jeol FX90Q spectrometer in solutions in deuteriochloroform using the $CDCl_3$ resonance (at δ_C 76.9 p.p.m. from Me_4Si) as internal reference. Rotations were taken in chloroform solution on a Thorn Automation-NPL type 234 automatic polarimeter. Mass spectra were recorded on a single-focusing AEI MS-12 mass spectrometer (Kratos Ltd., Manchester, U.K.) operated at accelerating voltage 8 kV, trap current 100 μA, ionization energy 70 eV, and ion source temperature 100 °C. Samples were introduced by the direct-insertion probe. Exact mass measurements were performed by computer processing at a resolving power (10% valley) of 9 000 using perfluorokerosene as the mass standard with a double-focusing AEI MS-902 S mass spectrometer (Kratos Ltd.) equipped with a VG-2020 data system. Light petroleum refers to that fraction boiling in the range 40—60 °C.

3β-*Methyl*-5α-*cholestan*-3α-*ol* (**1a**) *and* 3α-*Methyl*-5α-*cholestan*-3β-*ol* (**1b**).—The alcohols were prepared from cholestan-3-one (5.29 g) and methylmagnesium iodide as described previously.[1] Purification by column chromatography on silica gel with $CHCl_3$ as eluant, and crystallization from ethanol, yielded compound (**1a**) (3.054 g, 56%); R_F [benzene–EtOAc (9:1)] 0.36; m.p. 125 °C (lit.,[1] 126—127 °C); $[\alpha]_D^{20}$ +23.6 (*c* 0.89 in $CHCl_3$). Compound (**1b**) (2.324 g, 42%); R_F [benzene–EtOAc (9:1)] 0.17; m.p. 146 °C (lit.,[1] 147—148 °C); $[\alpha]_D^{20}$ + 32.0 (*c* 1.86 in $CHCl_3$).

3α-*Chloro*-3β-*methyl*-5α-*cholestane* (**2a**).—(*a*) Compound (**2a**) was prepared by reaction of alcohol (**1a**) or (**1b**) with HCl in dioxane as described before.[1] The crystalline product which was formed in the reaction was filtered off and recrystallized from light petroleum. Compound (**2a**) had R_F (n-hexane) 0.48; m.p. 148 °C (lit.,[1] 154—156 °C); $[\alpha]_D^{20}$ +27.7 (*c* 3.85 in $CHCl_3$) [Found: *m/z*, 420.3530 (M^+). Calc. for $C_{28}H_{49}Cl$: *M*, 420.3522]; $\nu_{max.}(CS)_2$ 782 and 560 cm^{-1}. Further purification of the mother liquor by column chromatography on silica gel with n-hexane as eluant afforded the other epimer (**2b**) in low yield (10%). This product was identical with the substance described below.

(*b*) To a stirred solution of 3α-methyl-5α-cholestan-3β-ol (**1b**) (180 mg, 0.45 mmol) and a 1.0M solution of $TiCl_4$ in CH_2Cl_2 (1 ml) in CH_2Cl_2 (15 ml) at room temperature and under N_2 was added dropwise with a syringe a solution of *NN*-dimethyl-(1-chloro-2-methylprop-1-enyl)amine (1 mmol) in CH_2Cl_2 (1.34 ml). After being stirred for 1 h, the reaction mixture was poured into water (20 ml). The organic layer was separated, washed with water (2 × 20 ml), and dried ($MgSO_4$). After the organic solvent was removed, the solid residue was recrystallized from light petroleum to afford chloride (**2a**) (166 mg, 88%), identical with the product obtained in method *a*.

3β-*Chloro*-3α-*methyl*-5α-*cholestane* (**2b**).—A solution of anhydrous $ZnCl_2$ (280 mg) in dry CH_2Cl_2 (30 ml) was added to a stirred solution of alcohol (**1a**) (240 mg, 0.58 mmol) in dry CH_2Cl_2 (10 ml). A solution of *NN*-dimethyl-(1-chloro-2-methylprop-1-enyl) (60 mg) in CH_2Cl_2 (0.6 ml) was added dropwise with a syringe and the mixture was stirred at room temperature under N_2 for 35 min. The reaction was quenched with MeOH (10 ml) and the mixture was washed with water (3 × 15 ml). The CH_2Cl_2 layer was dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was purified by column chromatography with n-hexane as eluant to afford, after evaporation of the eluant, *chloride* (**2b**) as a white solid (150 mg, 60%); R_F (n-hexane) 0.40; $[\alpha]_D^{20}$ +28.6 (*c* 0.23 in $CHCl_3$); m.p. 112 °C; [Found: *m/z*, 420.3513 (M^+)]; $\nu_{max.}(CS_2)$ 790 and 690 cm^{-1}. The anhydro products (**5**) and (**7**) (80 mg, 35%) were also isolated in the ratio 4:1 (based on the n.m.r. spectrum); R_F (n-hexane) 0.87; δ_H 5.36—5.15 [vinyl proton of (**5**)] and 4.52 [methylene protons of (**7**)].

Replacing $ZnCl_2$ by $SnCl_4$ or $TiCl_4$ gave the same result. With Me_2AlCl, $SiCl_4$, $FeCl_3$, and $SbCl_3$ a poor conversion of the alcohol was observed.

3α-*Fluoro*-3β-*methyl*-5α-*cholestane* (**3a**).—To a solution of DAST (0.2 ml, 1.2 mmol) in CH_2Cl_2 (1 ml) cooled to −70 °C was added dropwise a solution of alcohol (**1b**) (120 mg, 0.29 mmol) in CH_2Cl_2 (1.2 ml). The mixture was stirred for 15 min and then warmed to 0 °C. Water (0 °C; 3 ml) was added, and the CH_2Cl_2 layer was separated, washed with water (2 × 5 ml), and dried ($MgSO_4$). After evaporation of the solvent, the residue was crystallized from MeOH to afford pure *fluoride* (**3a**) (121 mg, 98%); R_F (n-hexane) 0.32; m.p. 135 °C; $[\alpha]_D^{20}$ +26.0 (*c* 0.62 in $CHCl_3$); [Found: *m/z*, 404.3796 (M^+). $C_{28}H_{49}F$ requires *M*, 404.3818]; $\nu_{max.}$(KBr) 866 cm^{-1}.

3β-*Fluoro*-3α-*methyl*-5α-*cholestane* (**3b**).—Alcohol (**1a**) (0.5 g, 1.2 mmol) was treated with DAST in the same way as described for the preparation of fluoride (**3a**). The residue obtained after evaporation of the solvent was purified by column chromatography on silica gel with n-hexane as eluant. This afforded the anhydro products (**5**), (**6**), and (**7**) (0.3 g, 60%) (80:15:5 as determined by n.m.r. spectroscopy); R_F 0.87 (hexane), the 3α-fluoro epimer (**3a**) (35 mg, 6.8%); R_F 0.32 (hexane), and the *title compound* (**3b**) (72 mg, 14%) as a white solid after evaporation of eluant; R_F (n-hexane) 0.22; m.p. 104 °C; $[\alpha]_D^{20}$ +25.4 (*c* 5.33 in $CHCl_3$) [Found: *m/z*, 404.3800 (M^+)]; $\nu_{max.}$(KBr) 892 cm^{-1}.

3α-*Acetoxy*-3β-*methyl*-5α-*cholestane* (**4a**).—Acetic anhydride (0.1 ml) was added to a stirred solution of alcohol (**1a**) (120 mg, 0.29 mmol) in CH_2Cl_2 (2 ml) containing DMAP (20 mg) and triethylamine (0.1 ml). After being kept at room temperature for 36 h the reaction mixture was washed successively with saturated aqueous sodium carbonate (1 × 5 ml) and water (3 × 5 ml). The solvent was removed under reduced pressure and, after having been kept for 24 h at room temperature, the residual oil crystallized to afford the ester (**4a**) (110 mg, 82%), R_F (benzene) 0.32; m.p. 79—81 °C; $[\alpha]_D^{20}$ +24.6 (*c* 1.83 in $CHCl_3$).

3β-*Acetoxy*-3α-*methyl*-5α-*cholestane* (**4b**).—The ester was prepared by the same procedure as described for its epimer (**4a**); R_F (benzene) 0.28; m.p. 84—86 °C; $[\alpha]_D^{20}$ +20.4 (*c* 1.92 in $CHCl_3$).

3-*Methyl*-5α-*cholest*-2-*ene* (**5**).—To a stirred solution of 3β-methyl-5α-cholestan-3α-ol (**1a**) (120 mg, 0.29 mmol) in acetic acid (6 ml) was added perchloric acid (70%; 6 drops). After the reaction mixture had been heated on a steam-bath for 30 min, water (30 ml) was added. The mixture was extracted with $CHCl_3$ (3 × 20 ml). The combined $CHCl_3$ layers were washed with water until neutral. After evaporation of the chloroform, the residue was crystallized from $CHCl_3$–MeOH (109 mg, 95%); R_F (n-hexane) 0.87; m.p. 80—81 °C (lit.,[1] 82—83 °C); $\delta_H(CDCl_3)$ 5.36—5.12 (br, 2-H).

Treatment of the epimeric alcohol (**1b**) in the same way as described above afforded the alkene (**5**) in the same yield.

3-*Methylene*-5α-*cholestane* (**7**).—Triphenylmethylphosphonium bromide (2.77 g) was shaken with butyl-lithium (3.3 ml; 15% in hexane) in dry ether (46 ml) for 3 h. Cholestan-3-one (2.0

g) was added and the solution was refluxed overnight. The solid precipitate was filtered off, washed with water, and further purified by crystallization from $CHCl_3$–MeOH to give the alkene (7) (0.9 g, 45%); R_F (n-hexane) 0.85; m.p. 61 °C (lit.,[1] 65—66 °C); $\delta_H(CDCl_3)$ 4.52 (s, $=CH_2$).

Conversion of the 3-*Methyl-5α-cholestanols* (**1a**) *and* (**1b**) *into the Olefins* (**5**), (**6**), *and* (**7**).—Phosphorus trichloride oxide (1 ml) was added dropwise (10 min) to a stirred solution of 3β-methyl-5α-cholestan-3α-ol (**1a**) (120 mg, 0.29 mmol) in dry pyridine (13 ml) at room temperature. After being kept for 24 h the reaction mixture was poured onto crushed ice, extracted with chloroform (3 × 15 ml), and washed with water until neutral. The organic extract was dried ($MgSO_4$) and evaporated under reduced pressure. The residue was crystallized from ethanol to afford a mixture of alkenes (**5**), (**6**), and (**7**) (62:23:15) (109 mg, 94%); R_F (n-hexane) 0.87; ($CDCl_3$) 5.12—5.36 [br, 2-H of (**5**)], 4.90—5.02 [br, 4-H of (**6**)], and 4.52 [s, methylene protons of (**7**)]. Similar treatment of 3α-methyl-5α-cholestan-3β-ol (**1b**) (120 mg, 0.29 mmol) gave a mixture (103 mg, 90%) of (**5**), (**6**), and (**7**) (23:11:66).

Reaction with Ph_3P–CCl_4.—A solution of triphenylphosphine (200 mg, 0.52 mmol) in CCl_4 (0.5 ml) was added to a solution of 3β-methyl-5α-cholestan-3α-ol (**1a**) (120 mg, 0.29 mmol) in dimethylformamide (6 ml) at room temperature. After the mixture had been kept for 24 h, the solvent was removed under reduced pressure. Water was added (10 ml) and the aqueous mixture was extracted with dichloromethane (3 × 10 ml). After removal of CH_2Cl_2 under reduced pressure, the residue was crystallized from ethanol to afford a mixture (100.9 mg, 88%) of the olefins (**5**), (**6**), and (**7**) (70:24:6), R_F (n-hexane) 0.87; $\delta_H(CDCl_3)$ 5.12—5.36 [br, 2-H of (**5**)], 4.90—5.02 [br, 4-H of (**6**)], and 4.52 [s, methylene protons of (**7**)].

Treatment of 3α-methyl-5α-cholestan-3β-ol (**1b**) (120 mg, 0.29 mmol) in the same was as described above gave a mixture (100 mg, 88%) of olefins (**5**), (**6**), and (**7**) (22:8:70).

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