# A-Substituted 5β-Steroids. VII. The Polyhalogenation of 5β-Cholestan-2-one

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The polyhalogenation of 5β-cholestan-2-one (I) in acetic acid containing hydrogen halide occurs in this positional order: $C_1 \rightarrow C_3 \rightarrow C_3$ and finally at $C_1$, which has the largest steric hindrance. The tetrahalogenation of the ketone (I) yields 1,1,3,3-tetrachloro-5β-cholestan-2-one (IXb), but fails to give the tetrabromo derivative; rather, it yields 1β,3,3-tribromo-5β-cholestan-2-one (Va), 1,1,3-tribromo-5β-cholest-3-en-2-one (VIIIa), and 1β,3-dibromo-5β-cholest-3-en-2-one (VIa). The conformations of the dihalo-, the trihalo-, and the tetrachloroketone derivatives are discussed in connection with the ORD, CD, IR, and NMR spectra.

Although the halogenation of most 5α-steroids[1] which possess an oxo group on each position in Ring A has been thoroughly investigated, only very little information on 5β-steroids is found in the literature, and even this concerns only the bromination of 3-oxo-5β-steroids.[2] We reported earlier that the monohalogenation of 2-oxo-5β-steroids affords the 1β-halo-2-oxo-5β-steroids[3] in good yields.

In this paper, we would like to discuss the positional order of the halogens introduced, and the conformation of the haloketones produced by the polyhalogenation of 5β-cholestan-2-one.

## Results and Discussion

The dibromination of 5β-cholestan-2-one (I) in acetic acid in the presence of hydrogen bromide gave the dibromo Compound A (mp 182—185 °C) and, from the filtrate, the dibromo Compound B (mp 155—156 °C). Compound A was epimerized by treatment with hydrogen bromide in acetic acid at room temperature to the stable Compound B. These dibromo derivatives showed shifts of the carbonyl absorption (+3 and +18 $cm^{-1}$ respectively) compared with that of the parent ketone (I) in their IR spectra. The NMR spectra also showed a multiplet at $\tau$ 5.6—5.8, with a small half-band width ($W/2=$ 12 Hz) with an equatorial character, and at $\tau$ 4.20, with a large half-band width ($W/2=20$ Hz) of an axial character due to the $C_3$HBr. From these facts, the structures of the two dibromoketones were confirmed to be 1β,3β-dibromo-(IIIa) and 1β,3α-dibromo-5β-cholestan-2-one (IVa) respectively.

On the other hand, the dichlorination of 5β-cholestan-2-one (I) gave the dichloroketone (IVb) (mp 128—129 °C). This product was presumed to be 1β,3α-dichloro-5β-cholestan-2-one from the sign of the Cotton effect, $\Delta$[A]*-, and the $\Delta\lambda_1$**-values (+192 and +12 nm respectively compared with 5β-cholestan-2-one) in the ORD spectrum, the shift of the C=O stretching band (1745 $cm^{-1}$) in the IR spectrum, and the signal ($\tau$ 4.70, $W/2=20$ Hz) due to the $C_3$HCl in the NMR spectrum.

Also, by tlc, it was confirmed that, when a solution of bromine was slowly added to the ketone (I) in acetic acid containing hydrogen bromide to effect dibromination, 1β-bromoketone (IIa) was formed first, and then the dibromoketones.

Thus, these results show that, as was previously reported for the monohalogenation[3] of the ketone (I), in the case of dihalogenation also the halogen enters first at the $C_1$β-bond, and then at the $C_3$β-bond. The 1β,3β-dibromo derivative thus produced is epimerized to a more stable 1β,3α-dibromo derivative.

On the basis of these data, we shall now discuss the conformation of the dihaloketones. It is considered, from the shifts in the C=O absorption (+18 for IVa and +33 $cm^{-1}$ for IVb) compared with the ketone (I) in the IR spectra and from the pattern of the NMR spectra, that 1β,3α-dihaloketones (IV) exists as a chair conformation. This is supported by the signs of the Cotton effect, $\Delta$[A]*-(+248 for IVa and +192 for IVb) and the $\Delta\lambda_1$**-values (+13 and +12 nm respectively) in ORD. Further, it is generally presumed that, if the A ring assumes a chair conformation, the ORD curve of 1β,3β-dibromoketone (IIIa) exhibits a negative sign of the Cotton effect, in accordance with the Octant rule.[4] However, the ORD data ($\Delta$[A]*: +93 compared with 5β-cholestan-2-one) of this compound are unusual in view of this presumption. Hence, it is considered that this compound (IIIa) prefers a deformed conformation because of the 1 : 3-interaction between the $C_1$β-Br and the $C_3$β-Br. This was supported by showing the half-band width ($W/2=12$ Hz) due to the $C_3$–H and also by the shift of C=O ($\Delta\nu$ : +2 $cm^{-1}$) compared with that of 5β-cholestan-2-one in the IR spectrum.

In order to determine the position of the third halogen in the trihalogenation of 5β-cholestan-2-one (I), the ketone (I) was treated with 3 M bromine in acetic acid. The reaction mixture was then chromatographed on silica gel. Elution with *n*-hexane–benzene (10 : 1) gave the tribromoketone (Va) (mp 157—158 °C). It was determined to be 1β,3,3-tribromo-5β-cholestan-2-one by means of its NMR spectrum, which shows a singlet at $\tau$ 4.47 and no proton signal due to the $C_3$HX. The second fraction, eluted with the same solvent, gave the 1β,3α-dibromo derivative (IVa), while the last fraction, eluted with the same solvent, gave the unsaturated dibromoketone (VIa), which shows absorptions at 1708 (C=O) and 1611 $cm^{-1}$ (C=C) in its IR spectrum, as the main product. The NMR spectrum of VIa showed a singlet at $\tau$ 5.31 due to the proton at $C_1$, and a doublet at $\tau$ 3.12 due to the vinyl proton. Therefore, the derivative (VIa) was presumed to be 1β,3-dibromo-5β-cholest-3-en-2-one, which is formed by the elimination of hydrogen bromide from the 1β,3,3-tribromo derivative (Va). It was then demonstrated that the trichlorination of 5β-

* Molar dispersion contribution of the substituent.

** The difference (nm) between the first extremum of the derivative and that of the parent ketone.

cholestan-2-one gave 1β,3,3-trichloro-5β-cholestan-2-one (Vb).

From these results, it was concluded that the trihalogenation occurs at the $C_3$ position.

On the basis of the CD, ORD, and IR spectral data for Va and Vb ($\Delta$[A]*: −57, $\Delta$[θ]: −98, $\Delta\lambda_1$**: +14 nm, $\Delta\nu$: +42 $cm^{-1}$ and $\Delta$[A]*: −62, $\Delta$[θ]: −37, $\Delta\lambda_1$**: +14 nm, $\Delta\nu$: +31 $cm^{-1}$), it is considered that the conformation in the A ring of the trihaloketone is a considerably distorted boat form.

In a previous paper[5], we reported that 1β-halo-5β-cholestan-2-one (II) can not change to the 1α-isomer, probably because of the 1 : 3-interaction between the $C_1$-equatorial bond and the $C_9$–$C_{11}$ bond. Also, the steric hindrance at the $C_3$-position is considerably less than that at $C_1$, and its position has mobility. Consequently, the halogen in the 1β-haloketone rearranges to the allylic position.

In order to study the introduction of the fourth halogen at the position, which has a large steric hindrance, the ketone (I) was allowed to react with 4 M bromine in acetic acid containing hydrogen bromide at 20 °C for 48 hr. The reaction product did not give the tetrabromo derivative; rather, it yielded 1β,3,3-tribromoketone (Va) as the main product. This reaction at 85 °C for 1 hr gave 1β,3,3-tribromoketone (Va) and the unsaturated tribromoketone (VIIIa), showing absorptions at 1708 (C=O) and 1602 $cm^{-1}$ (C=C) in its IR spectrum. The NMR spectrum of VIIIa also showed a doublet ($J$=3.0 Hz) due to the vinyl proton. From these data, the unsaturated ketone (VIIIa) was presumed to be 1,1,3-tribromo-5β-cholest-3-en-2-one (VIIIa).

Under the same conditions, the chlorination of the ketone(I) yielded 1,1,3,3-tetrachloro-5β-cholestan-2-one (IXb). This structure was determined from the fact that no signal due to the CHX appeared in the NMR spectrum.

From the ORD, CD, and IR spectral data, it can be considered that the conformation of IXb in the A ring preferred a form that was considerably distorted and had no eclipsed conformation between the $C_1$β-X bond and the $C_{10}$–Me bond, as in the case of the trihaloketone, no 1 : 3-interaction between the $C_1$α-X bond and the $C_9$–$C_{11}$ bond, and no 1 : 3-interaction between the $C_1$–X bond and the $C_3$–X bond.

It is considered that this difference in the bromination and the chlorination has the following causes: in the case of the tetrabromo derivative, a possible explanation is that there is a large steric hindrance between the axial bromines at the $C_1$ and $C_3$ positions, and between the $C_9$–$C_{11}$ bond and $C_1$–α bond, than those in the case of tetrachloro derivative. This consideration is supported by the experimental fact that the bromination of 1β,3-dibromo-5β-cholest-3-en-2-one which no longer has the 1 : 3-interaction between the axial bromine at the $C_1$ and $C_3$ positions, occurs at the $C_1$ position.

On the basis of these results, it was concluded that the polyhalogenation of 5β-cholestan-2-one (I) in acetic acid containing hydrogen halide occurs in this positional order: $C_1 \rightarrow C_3 \rightarrow C_3$, and finally at $C_1$, with the largest steric hindrance in the A ring.

## Experimental

All the melting points are uncorrected. The IR, ORD, and CD spectra were measured using a Hitachi model 215 grating infrared spectrophotometer and two JASCO spectropolarimeters, models ORD/UV-5 and J-20, respectively. The NMR spectra were measured in carbon tetrachloride, with TMS as the internal standard, using a nuclear magnetic resonance spectrometer, Hitachi-Perkin Elmer R-20A.

*Dibromination of 5β-Chlestan-2-one (I).* I (1.0 g) in acetic acid (50 ml) was treated with bromine (0.91 g) in acetic acid (5 ml) containing a few drops of 48% hydrobromic acid at room temperature for 40 min. The reaction mixture was then taken up in ether, and the ether extracts were washed with a sodium hydrogen carbonate solution and water, dried, and evaporated. The crystallization of the residue from ethanol gave plates of IIIa (40 mg); mp 182—185 °C; IR (KBr): 1715 $cm^{-1}$; IR ($CCl_4$): 1716 $cm^{-1}$; ORD (*c*, 0.207, Di) at 21 °C: $[\alpha]_D$ +14°, $[\alpha]_{400}$ +125°, $[\alpha]_{356}$ +405° (peak), $[\alpha]_{325}$ 0° and $[\alpha]_{250}$ −935° (trough); CD (*c*, 0.207, Di) at 21 °C: $[\theta]_{325}$ +3465° (peak); NMR ($CCl_4$) τ: 5.67 (1H, s, $C_1$α-H) and *ca.* 5.6—5.8 (1H, m, $W/2$=12 Hz, $C_3$α-H). Found: C, 59.49; H, 7.93%. Calcd for $C_{27}H_{44}OBr_2$: C, 59.56; H, 8.14%.

From the mother liquor, recrystallization gave plates of IVa (360 mg); mp 155—156 °C; IR (KBr): 1730 $cm^{-1}$; IR ($CCl_4$): 1736 $cm^{-1}$; ORD (*c*, 0.190, Di) at 21 °C: $[\alpha]_D$ +105°, $[\alpha]_{400}$ +434°, $[\alpha]_{329}$ +2237° (peak), $[\alpha]_{300}$ +1868° (shoulder), $[\alpha]_{305}$ 0° and $[\alpha]_{283}$ −1947° (trough); CD (*c*, 0.169, Di) at 21 °C: $[\theta]_{308}$ +20610° (shoulder) and $[\theta]_{303}$ +21040° (peak); NMR ($CCl_4$) τ: 5.64 (1H, s, $C_1$α-H) and 4.20 (1H, m, $W/2$=20 Hz, $C_3$β-H). Found: C, 59.34; H, 8.08%. Calcd for $C_{27}H_{44}OBr_2$: C, 59.56; H, 8.14%.

*Isomerization of 1β,3β-Dibromo-5β-cholestan-2-one (IIIa).* IIIa (10 mg) in acetic acid (5 ml) was stirred with a few drops of 48% hydrobromic acid at room temperature for 15 hr. After the usual work-up, crystallization from ethanol afforded plates of IVa (6 mg); mp 155—156 °C.

*Tribromination of 5β-Cholestan-2-one (I).* I (800 mg) in acetic acid (40 ml) was treated with bromine (1.09 g) in acetic acid (4 ml) at room temperature. After 17 hr, decolorization was complete; the reaction mixture was then taken up in ether, and the ether extracts were washed with a sodium hydrogen carbonate solution and water, dried, and evaporated. The resultant oil (1.225 g) was chromatographed on silica gel (100 g). Elution with *n*-hexane–benzene (10 : 1) (400 ml) gave needles of Va (41 mg) from ethanol; mp 157—158 °C; IR (KBr): 1747 $cm^{-1}$; IR ($CCl_4$): 1756 $cm^{-1}$; ORD (*c*, 0.150, Di) at 19.5 °C: $[\alpha]_D$ +33°, $[\alpha]_{400}$ +87°, $[\alpha]_{373}$ 0°, $[\alpha]_{370}$ −6.7° (trough), $[\alpha]_{367}$ 0°, $[\alpha]_{324}$ +1223° (peak), $[\alpha]_{299}$ 0° and $[\alpha]_{281}$ −588° (trough); CD (*c*, 0.111, Di) at 22 °C: $[\theta]_{347}$ −2328° (trough), $[\theta]_{330}$ 0° and $[\theta]_{303}$ +5611° (peak); NMR ($CCl_4$) τ: 5.68 (1H, s, $C_1$α-H). Found: C, 52.03; H, 6.90%. Calcd for $C_{27}H_{43}OBr_3$: C, 52.03; H, 6.95%.

The next fraction, eluted by the same solvent (300 ml), on crystallization from ethanol gave needles of IVa (134 mg), while the last fraction, eluted with the same solvent (370 ml) and with benzene (400 ml), on crystallization from ethanol gave needles of VIa (287 mg); mp 186—189 °C; IR (KBr): 1695 and 1610 $cm^{-1}$; ORD (*c*, 0.220, Di) at 25 °C: $[\alpha]_D$ −20°, $[\alpha]_{400}$ −89°, $[\alpha]_{360}$ −282° (shoulder), $[\alpha]_{350}$ −341° (trough), $[\alpha]_{335}$ −150° (shoulder), $[\alpha]_{329}$ 0° and $[\alpha]_{280}$ +1592° (peak); CD (*c*, 0.164, Di) at 25 °C: $[\theta]_{338}$ −2330° (shoulder), $[\theta]_{328}$ −3174° (trough), $[\theta]_{320}$ −2667° (peak), $[\theta]_{316}$ −2755° (trough), $[\theta]_{290}$ 0° and $[\theta]_{264}$ +13070° (peak); $\lambda^{Di}_{max}$ 260 nm (ε 4,900); NMR ($CCl_4$) τ: 5.31 (1H, s, $C_1$α-H) and 3.12

(1H, d, $J$=3.0 Hz, $C_4$–H). Found: C, 60.08; H, 7.77%. Calcd for $C_{27}H_{42}OBr_2$: C, 59.79; H, 7.80%.

*Tetrabromination of 5β-Cholestan-2-one (I) at Room Temperature.* A solution of I (800 mg) in acetic acid (40 ml) was treated with bromine (1.452 g) according to the procedure described for the tribromination of I. After the usual work-up, the resultant oil, on crystallization from ethanol, gave needles of Va (451 mg); mp 157—159 °C. After the crystallization filtrate had been evaporated *in vacuo*, the resultant oil (602 mg) was chromatographed on silica gel (80 g). Elution with *n*-hexane–benzene (9 : 1) (1350 ml) gave needles of Va (81 mg) from ethanol; mp 154—157 °C. The second fraction, eluted with the same solvent (800 ml), on crystallization from ethanol gave IVa (42 mg); the third fraction, eluted with *n*-hexane–benzene (5 : 1) (1750 ml), on crystallization from ethanol gave VIa (124 mg) (mp 186—189 °C).

*Bromination of 1β,3-Dibromo-5β-cholest-3-en-2-one (VIa).* The bromination of VIa was carried out using the technique described for the synthesis of the 1β-bromoketone.[3] After the usual work-up, the resultant oil was chromatographed on silica gel (10 g). Elution with *n*-hexane–benzene (1 : 10) (330 ml) and with benzene (300 ml) gave needles of VIIIa (19 mg) from ethanol; mp 84—86 °C; IR (KBr): 1708 and 1605 $cm^{-1}$; ORD (*c*, 0.169 Di) at 25 °C: $[\alpha]_D$ −44°, $[\alpha]_{400}$ −288°, $[\alpha]_{340}$ −616° (shoulder), $[\alpha]_{294}$ −2272° (trough), $[\alpha]_{284}$ 0° and $[\alpha]_{250}$ +7558° (peak); CD (c, 0.182, Di) at 25 °C: $[\theta]_{443}$ +469° (peak), $[\theta]_{394}$ 0°, $[\theta]_{347}$ −2203° (trough), $[\theta]_{320}$ 0°, $[\theta]_{303}$ +2711° (peak), $[\theta]_{294}$ 0° and $[\theta]_{269}$ −12200° (trough); $\lambda_{max}^{Di}$ 266 nm (ε 3,800); NMR ($CCl_4$) τ: 3.22 (1H, d, $J$=3.0 Hz, $C_4$–H). Found: C, 52.43; H, 6.76 %. Calcd for $C_{27}H_{41}OBr_3$: C, 52.19; H, 6.65%.

*Tetrabromination of 5β-Chlestan-2-one (I) at 85 °C.* I (500 mg) in acetic acid (25 ml) was treated with bromine (908 mg) in the presence of 48% hydrobromic acid at 85 °C for 1 hr. After the usual work-up, the resultant oil (532 mg) was chromatographed on silica gel (100 g). Elution with *n*-hexane–benzene (10 : 1) (550 ml) gave needles of Va (77 mg) from ethanol (mp 154—157 °C). The next fraction, eluted with *n*-hexane–benzene (5 : 1) (600 ml), on crystallization from ethanol gave needles of VIIIa (98 mg) (mp 84—86 °C); the last fraction, eluted with *n*-hexane–benzene (3 : 1) (3200 ml), on crystallization from ethanol gave VIa (147 mg) (mp 186—189 °C).

*Dichlorination of 5β-Cholestan-2-one (I).* A mixture of I (2.0 g), chlorine gas (855 mg) in chloroform (10 ml), and acetic acid was carried out according to the procedure described for the synthesis of the 1β-chloroketone.[3] After the usual work-up, the resultant oil was chromatographed on silica gel (100 g). Elution with *n*-hexane gave plates of IVb (343 mg) from ethanol; mp 128—129 °C; IR (KBr): 1740 $cm^{-1}$; IR ($CCl_4$): 1737 $cm^{-1}$; ORD (*c*, 0.203, Di) at 26 °C: $[\alpha]_D$ +103°, $[\alpha]_{400}$ +370°, $[\alpha]_{328}$ +2069° (peak), $[\alpha]_{318}$ +1601° (shoulder), $[\alpha]_{304}$ 0°, $[\alpha]_{280}$ −1675° (trough); CD (*c*, 0.203, Di) at 26 °C: $[\theta]_{309}$ +12070° (peak), $[\theta]_{305}$ +11850° (trough) and $[\theta]_{302}$ +12070° (peak); NMR ($CCl_4$) τ: 5.65 (1H, s, $C_1\alpha$-H) and 4.20 (1H, m, $W/2$=20 Hz, $C_3\beta$-H). Found: C, 71.04; H, 9.36%. Calcd for $C_{27}H_{44}OCl_2$: C, 71.19; H, 9.73%. The next fraction, eluted with the same solvent (1300 ml), on crystallization from ethanol–acetone gave 1β-chloro-5β-cholestan-2-one (IIb) (253 mg) (mp 116—118 °C).[3]

*Trichlorination of 5β-Chlestan-2-one (I).* The trichlorination of I (800 mg) was carried out using the technique described for the synthesis of the 1β-chloroketone.[3] The resultant oil (1.01 g) was chromatographed on silica gel (100 g). From the first elution with *n*-hexane (2450 ml) and with *n*-hexane–benzene (5 : 1) (450 ml), Vb was obtained as needles (389 mg); mp 142—145 °C; IR (KBr): 1745 $cm^{-1}$; IR ($CCl_4$): 1745 $cm^{-1}$; ORD (*c*, 0.219, Di) at 19.5 °C: $[\alpha]_D$ −9.1°, $[\alpha]_{400}$ −37°, $[\alpha]_{330}$ −624° (trough), $[\alpha]_{322}$ −452° (peak), $[\alpha]_{318}$ −485° (trough), $[\alpha]_{310}$ 0° and $[\alpha]_{275}$ +1050° (peak); CD (*c*, 0.219, Di) at 19.5 °C: $[\theta]_{324}$ −2769° (trough), $[\theta]_{312}$ −5021° (trough), $[\theta]_{308}$ −4762° (peak) and $[\theta]_{302}$ −5242° (trough); NMR ($CCl_4$) τ: 5.68 (1H, s, $C_1\alpha$-H). Found: C, 66.02; H, 8.56%. Calcd for $C_{27}H_{43}OCl_3$: C, 66.18; H, 8.84%. The second fraction, eluted with *n*-hexane–benzene (1 : 1) (200 ml), on crystallization from ethanol gave plates of IVb (57 mg) (mp 128—129 °C).

*Tetrachlorination of 5β-Cholestan-2-one (I).* I (2.5 g) and concd hydrochloric acid (0.3 ml) in acetic acid (100 ml) were treated with chlorine gas in chloroform (10 ml) at 85 °C for 20 hr. After the usual work-up, the resultant oil (3.0 g) was chromatographed on silica gel (100 g); further treatment with *n*-hexane (500 ml) eluted a yellow oil, which, on crystallization from ethanol, gave needles of IXb (810 mg); mp 104—105 °C; IR (KBr): 1766 $cm^{-1}$; IR ($CCl_4$): 1765 $cm^{-1}$: ORD (*c*, 0.242, Di) at 19.5 °C: $[\alpha]_D$ +87°, $[\alpha]_{400}$ +253°, $[\alpha]_{332}$ +636° (peak), $[\alpha]_{304}$ 0° and $[\alpha]_{289}$ −178° (trough); CD (*c*, 0.242, Di) at 19.5 °C: $[\theta]_{311}$ 3537° (peak). Found: C, 61.66; H, 7.99%. Calcd for $C_{27}H_{42}OCl_4$: C, 61.84; H, 8.07%. The next fraction, eluted with the same solvent (2500 ml) and with *n*-hexane–benzene (7 : 3) (350 ml), on crystallization from ethanol gave needles of 1β,3-dichloro-5β-cholest-3-en-2-one (VIb) (56 mg); mp 147—149 °C; IR (KBr): 1700 and 1615 $cm^{-1}$; ORD (*c*, 0.096, Di) at 19.5 °C: $[\alpha]_D$ +41°, $[\alpha]_{460}$ 0°, $[\alpha]_{400}$ −131°, $[\alpha]_{364}$ −386° (shoulder), $[\alpha]_{360}$ −438° (trough), $[\alpha]_{353}$ −399° (peak), $[\alpha]_{345}$ −522° (trough), $[\alpha]_{335}$ −256° (peak), $[\alpha]_{322}$ −282° (trough), $[\alpha]_{324}$ 0°, $[\alpha]_{307}$ +418° (shoulder) and $[\alpha]_{274}$ +522° (peak); CD (*c*, 0.096, Di) at 19.5 °C: $[\theta]_{335}$ −2625° (shoulder), $[\theta]_{324}$ −3515° (trough), $[\theta]_{317}$ −2929° (peak) and $[\theta]_{313}$ −3046° (trough); $\lambda_{max}^{Di}$ 251 nm (ε 6,700); NMR ($CCl_4$) τ: 5.48 (1H, s, $C_1\alpha$-H) and 3.40 (1H, d, $J$=2.5 Hz, $C_4$–H). Found: C, 70.63; H, 9.33%. Calcd for $C_{27}H_{42}OCl_2$: C, 71.50; H, 9.33%.

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