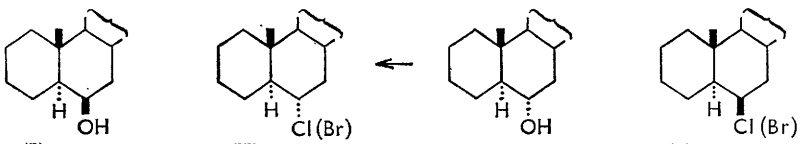
## 946. *Steroids and Walden Inversion. Part XLVI.* 6α-Chloro- and 6α-Bromo-5α-cholestane.*

By C. W. Shoppee, M. E. H. Howden, and Ruth Lack.

5α-Cholestan-6α-ol with the phosphorus pentahalides or thionyl halides yields 6α-chloro- and 6α-bromo-5α-cholestane, the retention of configuration being supported by infrared spectroscopy and molecular rotation differences.

These retentions of configuration are discussed and compared with the inversion, now demonstrated, on conversion of 5α-cholestane-3β,6α-diol into 3α,6β-dichloro-5α-cholestane by phosphorus pentachloride.

Some years ago Shoppee and Summers[1] attempted to prepare 6α-chloro-5α-cholestane (II) by treating 5α-cholestan-6β-ol[1,2] (I; 5α-H/6β-OH,*trans*, diaxial) with phosphorus pentachloride; the sole product was, however, 5α,6β-dichloro-5α-cholestane, which was believed to be formed by dehydration to cholest-5-ene and subsequent addition of chlorine derived from the equilibrium reaction, $PCl_5 \rightleftharpoons PCl_3 + Cl_2$.[3] We therefore attempted to obtain the 6α- (II) and 6β-halogeno-5α-cholestanes (IV) by treating 5α-cholestan-6α-ol[1,4,5] (III) with thionyl chloride or bromide, and with phosphorus pentachloride or pentabromide severally.




(I) (II) (III) (IV)

5α-Cholestan-6α-ol (III) with phosphorus pentachloride in benzene gave the 6α-chloro-compound (II) with retention of configuration: the infrared absorption spectrum exhibited peaks at 745 and 781 cm.$^{-1}$ corresponding with an equatorial carbon–chlorine stretching frequency, and a complete absence of bands in the 700—710 cm.$^{-1}$ region corresponding with an axial carbon–chlorine stretching frequency.[6,7] The chloride (II) is identical with the compound prepared by Stange[8] by the reaction of the alcohol (III) with phosphorus pentachloride only.

Professor D. H. R. Barton, F.R.S., has informed us (January 28th, 1958) that Mr. Pradhan, working in his laboratory in 1954, also found that 5α-cholestan-6α-ol (III) gave the chloro-compound (II) with both phosphorus pentachloride and thionyl chloride.

Stange's paper[8] contains an error, inasmuch as the observed rotation is given as −0·70°, whereas the specific rotation is given as +45°. This discrepancy was noticed by Barton and Miller,[9] who regarded the negative sign of the observed rotation as correct and leading to a specific rotation of −45°; they therefore formulated Stange's chloride as 6β-chloro-5α-cholestane (IV) on the grounds that the replacement of hydroxyl by chlorine with phosphorus pentachloride in saturated compounds normally leads to inversion of configuration,[10] and that 6β- are generally more lævorotatory than 6α-chloro-steroids (see below). Barton and Miller derived support for their formulation (IV) by determination of $[\alpha]_D$ +51°

* Part XLV, preceding paper.

[1] Shoppee and Summers, *J.*, 1952, 1786, 1790, 3361, 3374.
[2] Reich and Lardon, *Helv. Chim. Acta*, 1946, **29**, 675.
[3] Goering and McCarron, *J. Amer. Chem. Soc.*, 1956, **78**, 2270.
[4] Tschesche, *Ber.*, 1932, **65**, 1842.
[5] Karrer, Asmis, and Schwyzer, *Helv. Chim. Acta*, 1951, **34**, 1022.
[6] Barton, Page, and Shoppee, *J.*, 1956, 331.
[7] Cummins and Page, *J.*, 1957, 3847.
[8] Stange, *Z. physiol. Chem.*, 1933, **220**, 37.
[9] Barton and Miller, *J. Amer. Chem. Soc.*, 1950, **72**, 370.
[10] Shoppee, *J.*, 1946, 1138.

for a chloride, m. p. 150°, prepared by Heilbron [11] from 5α-cholestan-6α-ol (III) and thionyl chloride, which on account of its dextrorotation they regarded as 6α-chloro-5α-cholestane. We have also obtained this chloride, m. p. 149°, $[\alpha]_D$ +46°, in the same way, in poor yield, and it is identical with 6α-chloro-5α-cholestane (II).

It is possible that the secondary chloride, m. p. 91°, $[\alpha]_D$ +36°, isolated by Seng [12] from the mixture obtained by treatment of an ethereal solution of cholest-5-ene with ethanolic hydrogen chloride, may be a hydrate, not of 6β- (IV),[13] but of 6α-chloro-5α-cholestane (II); however, Barton and Schaeppi [14] were unable to confirm the formation of a 6-chloro-5α-cholestane under the conditions reported by Seng.[12]

5α-Cholestan-6α-ol (III) with phosphorus pentabromide in chloroform or in benzene gives, again with retention of configuration, 6α-bromo-5α-cholestane (II), m. p. 141—142°, $[\alpha]_D$ +50°, $\nu_{max.}$ 710 cm.$^{-1}$ (equatorial C–Br; subsidiary peaks at 724 and 753 cm.$^{-1}$; no bands at ~690 cm.$^{-1}$). This bromide is also obtained in poor yield from 5α-cholestan-6α-ol (III) by treatment with thionyl bromide, along with some 5α-cholestan-6α-yl sulphite.

All attempts to substitute halogen for hydroxyl in 5α-cholestan-6β-ol (I), using the thionyl halides and the phosphorus pentahalides under various conditions, resulted only in elimination to give cholest-5-ene.

The properties of the 6α-halogeno-5α-cholestanes (II), and of the 6β-epimers (IV) (see preceding paper) are summarised in Table 1.

TABLE 1.

| 6-Halogeno-5α-cholestane | M. p. | $[\alpha]_D$ | $\nu_{max.}$ (cm.$^{-1}$) | Halogen conformn. |
|---|---|---|---|---|
| 6α-Chloro- | 148° | +45° | 745, 781 | *eq* |
| 6β- ,, | 94 | −2 | 696 | *ax* |
| 6α-Bromo- | 142 | +50 | 710, 724 | *eq* |
| 6β- ,, | 125 | −16 | 665 | *ax* |

The infrared spectroscopic evidence quoted above is supported by molecular rotation differences for 5α-, 6α-, and 6β-chlorine and -bromine atoms (see Tables 2 and 3) which we have calculated from rotations recorded in the literature (except for 5-bromo-5α-cholestane [15]), using the standard Δ values of Barton and Klyne [16] and our own values for Δ3β-Cl and Δ3β-Br. The contributions of 5α-chlorine and 5α-bromine atoms are negative, namely, in the absence of vicinal action, −70° and −75°, respectively.

The contribution of a 6α-halogen atom is positive (Cl, +92°; Br, +135°), whilst that of a 6β-halogen atom is negative (Cl, −100°; Br, −163°), a difference in sign that appears to be characteristic of 6-substituents; in the A/B-*trans*-series Δ values for 6α-OH,[16] -OAc,[16] -$NH_2$,[17] and -NHAc [17] are +55°, +210°, +58°, and +175°, and for the 6β-analogues are −60°, −110°, −67°, and −141°, respectively. Table 3 shows that the Δ6α-Hal and Δ6β-Hal values agree (with one exception which is within the experimental error of ±10—15 units) amongst themselves in sign, and, in the absence of marked vicinal action, in magnitude. There can be no doubt that the configurations of the 6α- (II) and 6β-halides (IV) are correct.

Now, retention of configuration requires the operation of an intramolecular mechanism ($S_Ni$), involving a pyramidal transition state, which is promoted by electron-releasing groups and by conditions inhibiting ionisation; [18,19] retention of configuration in the conversion of 5α-cholestan-6α-ol (III) into the 6α-halogeno-5α-cholestanes (II) by both

[11] Heilbron, personal communication.
[12] Seng, Inaug. Diss., Göttingen, 1918, 29, 39.
[13] Georg, *Arch. Sci.*, 1953, **6**, 410.
[14] Barton, *Experientia*, 1955, Suppl. II, p. 128, footnote 2.
[15] Shoppee, Lack, and Howden, unpublished work.
[16] Barton and Klyne, *Chem. and Ind.*, 1948, 755.
[17] Shoppee, Evans, and Summers, *J.*, 1957, 97.
[18] Cowdray, Hughes, Ingold, Masterman, and Scott, *J.*, 1937, 1252.
[19] Dostrovsky, Hughes, and Ingold, *J.*, 1946, 186.

TABLE 2. Δ5α-Cl *and* Δ5α-Br *in the* 5α-*cholestane series.*

| Compound | M. p. | $[\alpha]_D$ | $[M]_D$ | Δ5α-Hal |
|---|---|---|---|---|
| 5α-*Chlorocholestane* | 96° | +5° | +21° | −70° |
| 5α-Chlorocholestan-3β-ol | 164 | +6 | +25 | −65 |
| 3β,5α-Dichlorocholestane | 117 | +12 | +53 | −57 |
| 5α-Chlorocholestan-6β-ol | 108 | −22 | −93 | −124 |
| 5α-Chlorocholestane-3β,6β-diol | 171 | −22 | −97 | −126 |
| 5α-Chlorocholestane-3β,6β-diol 3-acetate | 190 | −24 | −115 | −116 |
| 5α-Chlorocholestane-3β,6β-diol 3-benzoate | 130 | −20 | −108 | −150 |
| 5α-*Bromocholestane* | 80 | +4 | +16 | −75 |
| 5α-Bromocholestan-3β-yl acetate | 127 | +3 | +15 | −45 |
| 5α-Bromo-3β-chlorocholestane | 107 | +3 | +15 | −95 |
| 3β,5α-Dibromocholestane | 101 | +5 | +25 | −89 |
| 5α-Bromocholestan-6β-ol | 110 | −11 | −51 | −90 |
| 5α-Bromocholestane-3β,6β-diol | 128 | −38 | −184 | −220 |
| 5α-Bromocholestane-3β,6β-diol 3-acetate | 177 | −37 | −194 | −202 |
| 5α-Bromocholestane-3β,6β-diol 3-benzoate | 173 | −22 | −129 | −169 |

TABLE 3. Δ6α-Cl, Δ6β-Cl, Δ6α-Br, *and* Δ6β-Br *in the* 5α-*cholestane series.*

| Compound | M. p. | $[\alpha]_D$ | $[M]_D$ | Δ6-Hal |
|---|---|---|---|---|
| 6α-*Chloro*-5α-*cholestane* | 148° | +45° | +183° | +92° |
| 5α,6α-Dichlorocholestan-3β-ol | 172 | +2 | +9 | −10 |
| 5α,6α-Dichlorocholestan-3β-yl benzoate | 249 | +12 | +67 | +43 |
| 6β-*Chloro*-5α-*cholestane* | 94 | −2 | −8 | −100 |
| 6β-Chloro-5α-cholestan-3β-ol | 136 | −21 * | −89 | −178 |
| 3α,6β-Dichloro-5α-cholestane | 130 | +10 | +44 | −80 |
| 6β-Chlorocholestan-5α-ol | 119 | −6 | −25 | −64 |
| 6β-Chlorocholestan-3β,5α-diol | 173 | −8 | −35 | −72 |
| 6β-Chlorocholestan-3β,5α-diol 3-acetate | 191 | −27 | −128 | −120 |
| 5α,6β-Dichlorocholestane | 119 | −29 | −128 | −149 |
| 5α,6β-Dichlorocholestan-3β-ol | 143 | −27 | −123 | −142 |
| 5α,6β-Dichlorocholestan-3β-yl acetate | 89 | −29 | −145 | −155 |
| 5α,6β-Dichlorocholestan-3β-yl benzoate | 130 | −20 | −112 | −136 |
| 5α-Bromo-6β-chlorocholestan-3β-ol | 146 | −47 | −236 | −251 |
| 5α-Bromo-6β-chlorocholestan-3β-yl benzoate | 124 | −35 | −212 | −231 |
| 3β,5α,6β-Trichlorocholestane | 106 | −35 | −166 | −202 |
| 6α-*Bromo*-5α-*cholestane* | 141 | +50 | +225 | +135 |
| 6β-*Bromo*-5α-*cholestane* | 125 | −16 | −72 | −163 |
| 6β-Bromo-5α-cholestan-3β-ol | 112 | −9 | −42 | −131 |
| 6β-Bromo-5α-cholestan-3β-yl acetate | 141 | −29 | −146 | −206 |
| 6β-Bromo-5α-cholestan-3-one | 157 | −6 | −28 | −198 |
| 6β-Bromocholestan-5α-ol | 109 | −11 | −51 | −90 |
| 6β-Bromo-3β-chloro-5α-cholestane | 156 | −8 | −40 | −146 |
| 3β,6β-Dibromocholestane | 154 | −12 | −64 | −178 |
| 5α,6β-Dibromo-5α-cholestane | 106 | −40 | −212 | −228 |
| 5α,6β-Dibromocholestan-3β-ol | 114 | −44 | −240 | −254 |
| 5α,6β-Dibromocholestan-3β-yl acetate | 112 | −46 | −271 | −290 |
| 5α,6β-Dibromocholestan-3β-yl benzoate | 135 | −33 | −215 | −239 |
| 3β-Chloro-5α,6β-dibromocholestane † | 130 | −51 | −288 | −330 |
| 3β,5α,6β-Tribromocholestane | 112 | −51 | −311 | −350 |

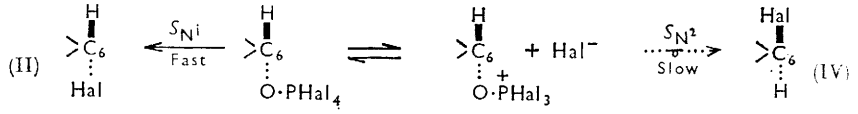
* $[\alpha]_{5461}$. † This compound has been found independently to have m. p. 133°, $[\alpha]_D$ −52° (Shoppee, unpublished data).

phosphorus pentahalides and thionyl halides is rational only if structural influences favour mechanism $S_Ni$ sufficiently to suppress mechanism $S_N2$.[20] In the case of 5α-cholestan-6α-ol the structural influences must be steric, not electronic or electrostatic, *i.e.*, repulsive exchange interactions following an inverse high-exponential function of distance at separations less than the sum of the van der Waals radii of the atoms concerned.[21] The fixed chair conformation of ring B hinders formation of the linear transition state at $C_{(6)}$ required for replacement of the equatorial 6α-hydroxyl group by mechanism $S_N2$; the axial 6β-hydrogen atom must become coplanar with the 5,6- and 6,7-bonds, and the halide ion must traverse a reaction co-ordinate close to the β-face of ring B and so encounter

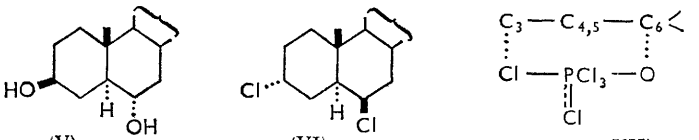
[20] Shoppee, *J.*, 1946, 1147.

[21] Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell and Son, London, 1953, pp. 33 *et seq.*

steric repulsion by the 4β- and 8β-hydrogen atoms and the 10β-methyl group. On the other hand, formation of a complex, R–O·$PCl_4$ or R–O·SOCl, by the equatorial 6α-hydroxyl group is subject only to 1,2-interactions with the 5α-, 7α-, and 7β-hydrogen atoms and the 4-methylene group, whilst the $S_Ni$ rearrangement of the complex is believed to be largely immune from steric retardation. Since the $S_N2$ mechanism is subject to steric retardation, the equilibrium furnishing ions derived from the complex may be rendered ineffective by the relative facility of the $S_Ni$ mechanism:




Of the numerous substituted 6β-halogeno-5α-cholestanes (Table 3), one is of special interest. By treatment of 5α-cholestane-3β,6α-diol [22–24] (V) with phosphorus pentachloride, Windaus [22] obtained a 3ξ,6ξ-dichloro-5α-cholestane, m. p. 128°, which Shoppee and Summers [1] regarded as 3α,6β-dichloro-5α-cholestane (VI). Dr. Summers has found for this compound (m. p. 130°, $[\alpha]_D$ +10°) a single, very intense, infrared band free from shoulders at 714 $cm.^{-1}$ (cf. 3α-chloro-5α-cholestane [6] 707, 6β-chloro-5α-cholestane 696, and other 6β-chloro-derivatives [6] 706—707 $cm.^{-1}$). Both chlorine atoms are therefore axial and structure (VI) is confirmed. Further proof comes from molecular rotation differences: The calculated specific rotations for the four 3,6-dichloro-5α-cholestanes are: 3α,6β-, +5°; 3β,6β-, +1°; 3α,6α-, +48°; 3β,6α-, +45°. So the reaction (V ⟶ VI) proceeds with




inversion of configuration at both positions 5 and 6. Some structural factor must intervene here so that mechanism $S_N2$, despite steric retardation, controls the situation; this factor must be associated with the 3α-chlorine atom. We suggest that replacement of the 3β-hydroxyl group of the diol (V) proceeds rapidly with inversion, that the 3α-chlorine atom so produced affects the orientation of the next-formed 6α-O·$PCl_4$ group by intramolecular bonding (cf. VII), and thus prevents mechanism $S_Ni$ operating whilst permitting mechanism $S_N2$ to proceed. Scale models show that such bonding is consistent with the molecular dimensions.

There is no insuperable steric hindrance to the introduction of a 6β-halogen atom (cf. Table 3). Kinetically controlled addition of halogens to the 5,6-double bond yields the diaxial 5α,6β-dihalides [9,25–27] which are also obtained [28] from the appropriate 5α-halogeno-6β-alcohols by treatment with either phosphorus pentachloride (or tribromide) or thionyl chloride; both the additions and the replacements may be formulated in terms of a covalent bromonium ion [28,29] or of a configurationally maintained 6-carbonium ion, but on either view the reaction co-ordinate traversed by the incoming halide anion must be closely similar to that of the chlorine anion in the reaction (V ⟶ VI). Kinetically controlled bromination of 3β-acetoxy-5α-cholestan-7-one yields the 6β-bromo-ketone; [30]

[22] Windaus, *Ber.*, 1917, **50**, 133.
[23] Marker, Jones, and Turner, *J. Amer. Chem. Soc.*, 1940, **62**, 2537.
[24] Plattner and Lang, *Helv. Chim. Acta*, 1944, **27**, 1872.
[25] Barton and Miller, *J. Amer. Chem. Soc.*, 1950, **72**, 1066.
[26] Barton and Rosenfelder, *J.*, 1951, 1048.
[27] Barton and Head, *J.*, 1956, 932.
[28] Barton, Miller, and Young, *J.*, 1951, 2598.
[29] Alt and Barton, *J.*, 1954, 4284.
[30] James and Shoppee, *J.*, 1956, 1064.

this also may be interpreted in terms of diaxial electrophilic addition to the enol with subsequent elimination of hydrogen bromide, or, preferably, as a consequence of the minimisation of the energy of the transition state of enolisation by maximum $2p\pi$-overlap of the *p*-orbital made available by the departing 6β(axial)[as opposed to the 6α(equatorial)]-proton and of the principle of microscopic reversibility [31] which requires the incoming brominium cation $Br^+$ to adopt the 6β-configuration and so to follow a reaction co-ordinate similar to that of the chlorine anion in the process (V—VI).

## Experimental

$[\alpha]_D$ are for $CHCl_3$ solutions; ultraviolet absorption spectra were measured for EtOH solutions on a Hilger Uvispek spectrophotometer, and infrared absorption spectra were determined for $CS_2$ solutions with a Perkin–Elmer model 21 double-beam instrument and sodium chloride prism, or as Nujol mulls with a potassium bromide prism.

6α-*Chloro*-5α-*cholestane*.—(*a*) 5α-Cholestan-6α-ol (m. p. 131°; 536 mg.) in benzene (50 ml.) was refluxed with phosphorus pentachloride (sublimed at 80°/2 mm.; 300 mg.) for 1 hr. After dilution the usual isolation procedure gave an oil (550 ml.), which was chromatographed on a column of neutralised aluminium oxide [32] (16 g.) prepared in hexane. Elution with hexane (3 × 50 ml.) afforded 6α-chloro-5α-cholestane (490 mg.), m. p. 146—148°, $[\alpha]_D$ +44° (*c* 1·1), $\nu_{max.}$ 745, 781 cm.$^{-1}$, after recrystallisation from acetone. A similar experiment in which the reactants were ground together in chloroform, furnished the same chloride, m. p. and mixed m. p. 148°, $[\alpha]_D$ +44° (*c* 1·0).

(*b*) The 6α-alcohol (200 mg.) in ether (20 ml.) was refluxed with purified thionyl chloride (0·55 ml.) for 3 hr. After addition of water, the product was isolated in the usual way as a solid (228 mg.), which by recrystallisation from acetone gave 6α-chloro-5α-cholestane (114 mg.), m. p. 148—149°, $[\alpha]_D$ +46° (*c* 0·9) (infrared absorption as above) (Found: C, 79·6; H, 11·6. Calc. for $C_{27}H_{47}Cl$: C, 79·7; H, 11·6%).

6α-*Bromo*-5α-*cholestane*.—(*a*) 5α-Cholestan-6α-ol (334 mg.) in benzene (30 ml.) was refluxed with phosphorus pentabromide (sublimed at 35°/0·5 mm.; 400 mg.) for 1 hr. to yield, after the usual working up, the 6α-*bromide* (442 mg.) (from acetone), m. p. 141—143°, $[\alpha]_D$ +48° (*c* 1·3), $\nu_{max.}$ 710, 753 cm.$^{-1}$ (Found: C, 71·7; H, 10·6. $C_{27}H_{47}Br$ requires C, 71·8; H, 10·5%).

(*b*) The 6α-alcohol (300 mg.), phosphorus pentabromide (370 mg.), and chloroform (1 ml.) were ground together; the mixture became deep red, then colourless after 5 min. After 30 min. ice was added, and the usual isolation procedure gave the above bromide (400 mg.) m. p. and mixed m. p. 141—142°, $[\alpha]_D$ +50° (*c* 1·35) (Found: C, 72·2; H, 10·3%).

(*c*) The 6α-alcohol (440 mg.) in ether (5 ml.) at 0° was treated with thionyl bromide (260 mg.) dropwise with stirring; after 15 min. at 0° and 30 min. at 20° the mixture was poured into water and worked up in the usual way to afford an oil. Dissolution in warm acetone gave di-5α-*cholestan*-6α-*yl sulphite* (20 mg.), m. p. 175—176° (from acetone) (Found: C, 79·1; H, 11·7; S, 4·0. $C_{54}H_{94}O_3S$ requires C, 78·8; H, 11·5; S, 3·9%). Concentration of the acetone solution furnished the above bromide (20 mg.), m. p. 141°, $[\alpha]_D$ +45° (*c* 0·9) (from acetone) (infrared absorption as above) (Found: C, 72·2; H, 10·4%). Chromatography of the residue from the acetone mother-liquors on neutralised aluminium oxide (12 g.) prepared in hexane, with elution by hexane (2 × 40 ml.), gave more of the bromide (40 mg.), m. p. 139—141°; then elution with ether–benzene) 1—4%) gave unchanged 5α-cholestan-6α-ol (138 mg.), m. p. 130°.

*Action of Phosphorus Pentabromide on* 5α-*Cholestan*-6β-*ol*.—5α-Cholestan-6β-ol [1] (m. p. 82—83°; 300 mg.), phosphorus pentabromide (370 mg.), and chloroform (1 ml.) were ground together and left for 0·5 hr. The usual working up gave only an oil (370 mg.); chromatography gave unsaturated material (probably mainly cholest-5-ene).

*Action of Thionyl Chloride on* 5α-*Cholestan*-6β-*ol*.—5α-Cholestan-6β-ol (388 mg., 0·001 mol.) in dry ether (10 ml.) was treated with freshly distilled thionyl chloride (0·08 ml., 0·0012 mol.) at 0° for 5 min. (cf. Kosower and Winstein [33]). After removal of the solvent at 20° in a vacuum, pentane (10 ml.) was added, and the solution filtered through calcium carbonate (500 mg.) and evaporated in a vacuum at 20°. The resulting white solid recrystallised from acetone on cooling

[31] Corey, *J. Amer. Chem. Soc.*, 1954, **76**, 175; cf. Djerassi, Finch, and Mauli, *ibid.*, 1959, **81**, 4997.
[32] Reichstein and Shoppee, *Discuss. Faraday Soc.*, 1949, **7**, 205.
[33] Kosower and Winstein, *J. Amer. Chem. Soc.*, 1956, **78**, 4347, 4354.

to −40° and gave nearly pure cholest-5-ene (290 mg.), m. p. 85°, $[\alpha]_D$ −52° (lit.,[34] m. p. 89°, $[\alpha]_D$ −56°) (Found: C, 86·3; H, 12·0. Calc. for $C_{27}H_{46}$: C, 87·3; H, 12·7%).

*Treatment of 5α-Cholestan-6α-ol with Hydrogen Chloride.*—5α-Cholestan-6α-ol (100 mg.) was recovered unchanged (90 mg.) when a solution in dry benzene (20 ml.) was treated with dry hydrogen chloride (or hydrogen bromide) for 1 hr. at 20° or 80°.

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[34] Mauthner, *Monatsh.*, 1894, **15**, 85.