The infrared spectrum of the carbinol showed a free OH band at 2.79 μ (sh), a broad hydrogen-bonded OH band at 3.00 μ, and C=C band at 6.135 μ.

Using the same procedure, 16.7 g. (0.066 mole) of ethyl(1,2-dichlorotetrafluorocyclobutyl)carbinol with 7 g. (0.11 g.-atom) of zinc dust gave 9.4 g. (0.051 mole, 78% yield) of ethyl (3,3-4,4-tetrafluoro-1-cyclobutenyl)carbinol, b.p. 98–100° (50 mm.).

Dehydration of Methyl(3,3,4,4-tetrafluoro-1-cyclobutenyl)-carbinol.—To 19 g. (0.13 mole) of phosphoric anhydride was added dropwise 15 g. (0.09 mole) of the carbinol and the reaction mixture was heated at 140° for 40 min. and distilled. Redistillation of the product gave 8.5 g. (0.056 mole, 63% yield) of 3,3,4,4-tetrafluoro-1-cyclobutenylethylene, b.p. 99–100°, $n^{20}D$ 1.3820. d^{20}_4 1.260 (lit.[1] b.p. 98–99°, $n^{25}D$ 1.3742, d^{25}_4 1.2588).

Anal. Calcd. for $C_6H_4F_4$: F, 50.0. Found: F, 49.7.

The tetrafluorocyclobutenylethylene was polymerized easily upon standing in the air or by peroxide treatment to give a transparent polymer.

Synthesis of 6β-(2,6-Dichlorobenzoyloxy)-2,4-cholestadiene and Related Compounds[1a]

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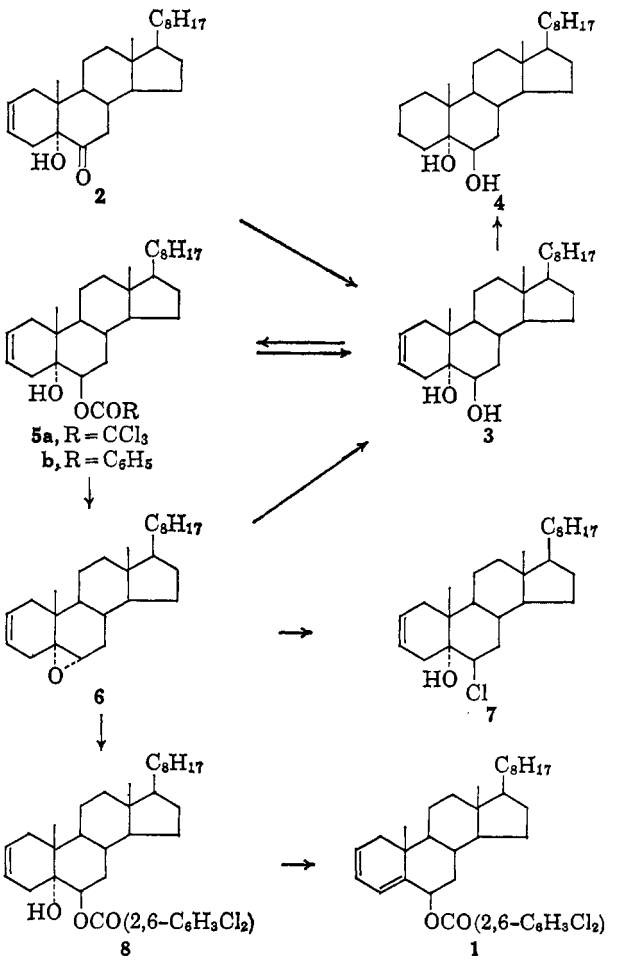
The preparations of 2-cholestene-5α,6β-diol (**3**) and two 6β ester derivatives are described. Treatment of the latter compounds with base yields 5α,6α-epoxy-2-cholestene, which may be converted to **3**, to 6β-chloro-2-cholsten-5α-ol, and to 6β-(2,6-dichlorobenzoyloxy)-2-cholesten-5α-ol. The latter ester, whose preparation by esterification of **3** with 2,6-dichlorobenzoyl chloride was unsuccessful, may be dehydrated to yield the title compound. Some aspects of the spectra of these compounds are discussed.

In connection with investigations of the direct and solvolytic nucleophilic displacement reactions of some conjugated dienes bearing suitable leaving groups in an allylic position, we required a convenient synthesis of 6β-(2,6-dichlorobenzoyloxy)-2,4-cholestadiene (**1**). This compound seems to be an appropriate substrate for observing long-range allylic rearrangements in a stereochemically well-defined system. The success of Summers, *et al.*,[2a,b] Wallis and Becker,[2c] and Young, *et al.*,[2d] in preparing 6β-substituted 4-cholestenes by dehydration of the corresponding 5α-cholestanols with thionyl chloride in pyridine prompted our investigation of the same reaction in the 2-cholestene series. The preparation and therapeutically interesting biological activities of Δ^2 steroids bearing appropriate substituents elsewhere in the molecule have been the subjects of recent reports.[3]

2-Cholesten-5α-ol-6-one (**2**) has been described by Reich, Walker, and Collins,[4] and appeared to be an appropriate entry to the desired system. We have repeated their preparation on a larger scale and have shown that material of adequate quality for our purposes may be obtained by crystallization rather than chromatography.

Treatment of the ketone **2** with lithium aluminum hydride afforded 2-cholestene-5α,6β-diol (**3**) (see Chart I) in excellent yield as a nicely crystalline solid. The assignment of the β configuration to the 6-hydroxyl group thus introduced is analogous to an example reported by Wallis and Becker[2c] who prepared cholestane-5α,6β-diol by lithium aluminum hydride reduction of cholestan-5α-ol-6-one. While lithium aluminum hydride reduction of 6-keto steroids gives predominantly the 6β-hydroxy steroid it is usually possible to isolate some of the 6α epimer.[5] In the present case, as in that of the corresponding reduction of cholestan-5α-ol-6-one,[2c] the normal preference for attack on the less hindered side is probably reinforced

CHART I



(1) (a) This work was supported by funds administered by the Research Committee, The Graduate School, Washington State University. (b) To whom communications should be addressed.

(2) (a) A. J. Fudge, C. W. Shoppee, and G. H. R. Summers, *J. Chem. Soc.*, 958 (1954); (b) D. N. Jones, J. R. Lewis, C. W. Shoppee, and G. H. R. Summers, *ibid.*, 2876 (1955); (c) E. J. Becker and E. S. Wallis, *J. Org. Chem.*, **20**, 353 (1955); (d) R. E. Ireland, T. I. Wrigley, and W. G. Young, *J. Am. Chem. Soc.*, **80**, 4604 (1958).

(3) For some recent examples and references to earlier work, see J. A. Edwards, P. G. Holton, J. C. Orr, E. Necoechea, A. de la Roz, E. Segovia, R. Urquiza, and A. Bowers, *J. Med. Chem.*, **6**, 174 (1963).

(4) H. Reich, F. E. Walker, and R. W. Collins, *J. Org. Chem.*, **16**, 1753 (1951).

(5) C. W. Shoppee and G. H. R. Summers, *J. Chem. Soc.*, 3361 (1952).

by initial reaction of the aluminohydride anion with the acidic proton of the 5α-hydroxyl group. In the resulting lithium alkoxyaluminohydride, intramolecular attack of the hydride on the 6-keto group can occur only from the α side of the molecule and must result in the β orientation of the 6-hydroxyl group thus introduced. This might be considered as an example of "approach control"[6] of the direction of reduction of a carbonyl group in which the control is exerted by preliminary bonding of the reducing species to the molecule as well as by steric effects. Further confirmation of this assignment of the β configuration to the 6-hydroxyl group was afforded by the hydrogenation of **3** to cholestane-5α,6β-diol (**4**), identified by comparison with an authentic sample.[4]

The sterically less hindered 6β-hydroxyl group in **3** is readily esterified by treatment with trichloroacetyl chloride or benzoyl chloride in pyridine, affording **5a** and **5b**. Attempts to esterify the 6β-hydroxyl group with the sterically hindered 2,6-dichlorobenzoyl chloride were unsuccessful under all conditions attempted. These conditions included refluxing the diol and acid chloride in pyridine overnight and reaction of the acid chloride with the sodium salt of the diol **3** (prepared with sodium hydride) in refluxing benzene. Examination of the infrared spectra of the crude products indicated that no appreciable conversion to ester had occurred.[7]

Another route to the desired 6β-(2,6-dichlorobenzoyloxy)-2-cholesten-5α-ol **8** was suggested by the observation that treatment of either **5a** or **5b** with methanolic potassium hydroxide yielded not only the expected saponification product **3**, but another product as well. The analysis of this compound was consistent with the molecular formula $C_{27}H_{44}O$. No infrared absorption bands suggestive of the presence of typical oxygen functions were observed, and the n.m.r. spectrum of the compound showed, in addition to the expected absorptions of the cholestane nucleus, a "hump" at 334 c.p.s. corresponding to two protons and attributed to the ethylenic protons at C-2 and C-3,[8] and a doublet centered at 169 c.p.s. with J = 3.8 c.p.s.[9] Since Cross has shown that steroidal 5α,6α epoxides typically show a doublet around 170 c.p.s. with J = 3.3–4.1 c.p.s.[10] and it has been observed that they usually exhibit no significant C–O infrared absorptions,[11] this compound is formulated as 5α,6α-epoxy-2-cholestene (**6**). This structure was confirmed by the facile periodic acid catalyzed opening of the oxirane ring to afford the *trans*-diol **3**, and by hydrogen chloride ring opening which gave 6β-chloro-2-cholesten-5α-ol (**7**).

Treatment of the epoxide **6** with 2,6-dichlorobenzoic acid in refluxing benzene smoothly opened the ring to give a good yield of the desired 6β-(2,6-dichlorobenzoyloxy)-2-cholesten-5α-ol (**8**). While such ring-opening reactions commonly afford *trans*-diol esters with formic acid and acetic acid,[12] they do not appear to have been exploited for the preparation of esters of other acids.[13] Although attack of the sterically hindered 6β-OH (or its sodium salt) of diol **3** on the sterically hindered carbonyl carbon of 2,6-dichlorobenzoyl chloride does not occur even under vigorous conditions, the epoxide ring-opening reaction does not involve any sp^2–sp^3 transformation of the carbonyl carbon of the acyl moiety and is thus less subject to steric retardation.

When the diol dichlorobenzoate **8** was treated with thionyl chloride in pyridine solution, a noncrystalline product was obtained which is assigned structure **1** on the basis of its mode of formation, the agreement of elemental analysis with the formula $C_{34}H_{46}Cl_2O_2$, and infrared, ultraviolet, and n.m.r. spectra. Wallis[2c] and Summers[2a,b] have established that dehydration of esters of other steroidal 5α alcohols proceeds to give the Δ^4 steroid when the 6β position is substituted by an oxygen function, a reaction which would give the 2,4-diene in this case. The ultraviolet spectrum of the product exhibits an absorption at 267 mμ (ε 5100), while Skau and Bergmann[14] report λ_{max} 267 (ε 6300) and 275 mμ, for 2,4-cholestadiene. More recently, a series of steroid 2,4-dienes have been prepared exhibiting an absorption at 266 mμ with (ε 6000–6400).[8] The infrared spectrum, which is consistent with the formulation of the product as **1**, shows no absorption at 2.78 μ, where the hydroxy ester **8** absorbs. Also, the strong absorption at 15.0–15.1 μ, which is present in all 2-cholestene derivatives in this series, is replaced in **1** by a strong absorption at 14.35 μ and a weaker one at 13.70 μ. We have also observed these latter absorptions in 2,4-cholestadien-6-one.[4] Absorption in the ranges 14.2–14.6 and 13.7–13.9 μ has been observed in the 2,4-dienes reported by Berkoz, *et al.*[8] The n.m.r. spectrum shows, in addition to the usual cholestane nucleus absorptions and a 3-proton resonance at 434 c.p.s. due to the dichlorobenzoyl protons, a complex 4-proton resonance between 330 and 420 c.p.s. assigned to the three ethylenic protons and the allylic α-proton at C-6.

More complete characterization of the diene dichlorobenzoate **1** is made difficult by its limited stability. Attempts to crystallize it from polar solvents have led to materials whose ultraviolet spectra (absorption at 234 mμ) suggest substantial solvolysis and rearrangement to compounds possessing a 3,5-diene chromophore, and it is very soluble in nonpolar solvents. Also, the compound appears to have a limited shelf life since storage for 3 months at ambient conditions leads to virtual disappearance of the absorption at 267 mμ. We are currently investigating the behavior of this substance with nucleophiles under both solvolytic and direct displacement conditions.

Some aspects of the spectra of these compounds are of interest in addition to those discussed above. The n.m.r. spectra of all compounds in this series

(6) W. G. Dauben, G. J. Fonken, and D. S. Noyce, *J. Am. Chem. Soc.*, **78**, 2579 (1956).

(7) The low degree of reactivity of 2,6-dichlorobenzoyl chloride was further emphasized by the incidental observation that it may be eluted unchanged from acid-washed alumina.

(8) B. Berkoz, A. D. Cross, M. E. Adame, H. Carpio, and A. Bowers, *J. Org. Chem.*, **28**, 1976 (1963).

(9) N.m.r. spectra were obtained with a Varian A-60 instrument at 60 Mc. on 10% w./v. solutions in CCl_4. Frequencies are in cycles per second downfield from the tetramethylsilane reference.

(10) A. D. Cross, *J. Am. Chem. Soc.*, **84**, 3207 (1962).

(11) H. H. Günthard, H. Hessler, and A. Fürst, *Helv. Chim. Acta*, **36**, 1900 (1953).

(12) J. G. Phillips and V. O. Parker in "Steroid Reactions," C. Djerassi, Ed., Holden-Day, Inc., San Francisco, Calif., 1963, Chapter 14.

(13) For an example of such a reaction in the lanostane series which involves a *cis* ring opening to give a benzoate ester, probably by way of an allylic carbonium ion, see P. A. Mayor and G. D. Meakins, *J. Chem. Soc.*, 2792 (1960).

(14) E. L. Skau and W. Bergmann, *J. Org. Chem.*, **3**, 166 (1938).

possessing the 2-cholestene nucleus show the 2-proton "hump" centered at 333–336 c.p.s. characteristic of the olefinic protons in this structural unit.[8] The positions of the 18- and 19-methyl group resonances in these compounds are recorded in Table I, along

TABLE I
N.M.R. FREQUENCIES OF THE ANGULAR METHYL GROUPS AND 6-PROTONS OF 2-CHOLESTENE DERIVATIVES[a]

Compd.	18-H	19-H	6-H[b]
1	39	59	*c*
2	41	41	...
3	41	59	212
4	41	57	203
5a	39	62	288
5b	41	69	302
6	40	63	169
7	42	66	230
8	39	~53	299

[a] Footnote 9. [b] 6-Proton orientation α in all except 6. [c] See text.

with those due to the 6-proton. The latter resonances, except for that of the epoxide **6**, show a half-band width of 5–7 c.p.s., consistent with the α orientation of these protons.

A comparison of the infrared spectra of 2-cholesten-5α,6β-diol (**3**) and its derivatives indicates that the 5α-hydroxyl function in **3** is hydrogen bonded to the π-electrons of the C-2–C-3 double bond. Thus the spectrum of **3** exhibits two sharp absorptions at 2.76 and 2.78 μ whose relative intensity is concentration independent. Esterification of the 6β-hydroxyl function results in the loss of the 2.76-μ absorption but does not alter the 2.78-μ peak. Hydrogenation of the double bond causes the peak at 2.78 μ to coincide with the 2.76-μ peak. The shift of 28 ± 3 cm.$^{-1}$ is consistent with this type of interaction.[15,16] Since many simple homoallylic alcohols do not exhibit such hydrogen bonding,[17] its appearance in this system must be attributed to favorable spatial relationships in the conformationally rigid steroid nucleus.

Experimental[18]

3β-*p*-Toluenesulfonyloxycholestan-5a-ol-6-one.—Cholestane-3β,5α-diol-6-one[19] (29.9 g., 71.5 mmoles) was treated with *p*-toluenesulfonyl chloride (15 g., 79 mmoles) in 90 ml. of pyridine according to the procedure of Reich, Walker, and Collins.[4] On this scale, isolation of the product by crystallization from acetone–hexane was more convenient than chromatographic purification and afforded 25.4 g. (62%) of crystalline product, m.p. 156–159 dec. (lit.[4] m.p. 161–163° dec.), of adequate purity for subsequent steps.

2-Cholesten-5α-ol-6-one (2).—A solution of 3β-tosyloxycholestan-5α-ol-6-one (53 g., 93.5 mmoles) in 1600 ml. of dry pyridine was refluxed for 24 hr. The pyridine was then evaporated with gentle warming at 0.5-mm. pressure. The residue was extracted with four 250-ml. portions of ether. The ether extract was washed three times with 5% aqueous hydrochloric acid and once with 5% aqueous sodium bicarbonate. After drying the solution over sodium sulfate, the ether was evaporated and the residue was recrystallized twice from methylcyclohexane, affording 13.2 g. (35%) of crystalline product, m.p. 139–140° (lit.[4] m.p. 140–141.5°), $[\alpha]^{25}D$ −27° (*c* 2, absolute ethanol) (lit.[4] $[\alpha]^{26}D$ −25.1 ± 3°), of adequate quality for subsequent steps.

2-Cholestene-5α,6β-diol (3).—A solution of 2-cholesten-5α-ol-6-one (10.0 g., 2.5 mmoles) in 100 ml. of dry ether was added dropwise to a stirred slurry of lithium aluminum hydride (900 mg., 2.4 mmoles) in 150 ml. of ether. After the addition was complete, the mixture was stirred for 3 hr., when water (2 ml.) was added dropwise with caution, followed by 10% aqueous sodium hydroxide (1.6 ml.). The mixture was stirred for 1 hr. and filtered from the inorganic salts. The filtrate was evaporated and the residue was recrystallized twice from methylcyclohexane, affording 9.1 g. (90.5%) of crystalline **3**, m.p. 134–135°. The analytical sample was prepared by two further crystallizations from hexane: m.p. 133.8–134.5°; $[\alpha]^{25}D$ +20; infrared bands at 2.76, 2.78, 2.85 (broad), 3.31, and 15.0 μ. The infrared spectrum taken on a 1% solution in CCl_4 (1.0-mm. path length) was identical except that the 2.85-μ band had disappeared and the 2.76- and 2.78-μ bands were increased in intensity.

Anal. Calcd. for $C_{27}H_{46}O_2$: C, 80.54; H, 11.52. Found: C, 80.45; H, 11.50.

Cholestane-5α,6β-diol (4).—A solution of 2-cholestene-5α,6β-diol (**3**, 400 mg., 1.0 mmole) in 25 ml. of 95% ethanol was quantitatively reduced over a platinum oxide catalyst in a Brown hydrogenation apparatus. The mixture was filtered by suction and the solvent was removed under reduced pressure to yield a clear glass which was taken up in ether. Removal of the ether under reduced pressure gave a white crystalline solid, m.p. 115–115.8° (lit.[4] m.p. 116–118°). After recrystallization from hexane it had m.p. and m.m.p. (with an authentic sample[4]) 123.5–124.5° (lit.[4] m.p. 123.5–126.5°)[20]; $[\alpha]^{22}D$ −3° (lit.[2b] $[\alpha]D$ −3°); infrared bands at 2.76, 6.82, 7.26, 9.57, and 10.38 μ, identical with those of the authentic sample.

6β-Benzoyloxy-2-cholesten-5α-ol (5b).—To a solution of 2-cholestene-5α,6β-diol (**3**, 402 mg., 1.0 mmole) in 10 ml. of dry pyridine was added benzoyl chloride (280 mg., 2.0 mmoles). After 20 hr. at room temperature, the cherry red solution was poured into 30 g. of ice and the resulting aqueous mixture was extracted with 30 ml. of ether. The ether extracts were washed with successive 50-ml. portions of 5% aqueous hydrochloric acid, 5% aqueous sodium bicarbonate, and water. After drying the solution over sodium sulfate, the ether was evaporated. The residue crystallized upon trituration with 95% ethyl alcohol. One crystallization from ethyl alcohol afforded 425 mg. (84%), m.p. 122.3–125.1°. The analytical sample was prepared by three further crystallizations from 95% ethyl alcohol: m.p. 123.7–125.3°; $[\alpha]^{25}D$ +28°; infrared bands at 2.78, 2.85, 3.31, 5.82, 7.89, and 15.02 μ.

Anal. Calcd. for $C_{34}H_{50}O_3$: C, 80.58; H, 9.95. Found: C, 80.37; H, 9.78.

6β-Trichloroacetoxy-2-cholesten-5α-ol (5a).—A solution of 2-cholestene-5α,6β-diol (**3**, 5.0 g., 12 mmoles) in 50 ml. of pyridine was treated with trichloroacetyl chloride (2.39 g., 13.2 mmoles) and the mixture was allowed to stand for 12 hr. at room temperature. The yellow-brown solution was worked up in the same manner as in the preparation of the benzoate. Two crystallizations from methanol afforded 2.4 g. (37%), m.p. 94.1–95.3°. The analytical sample was prepared by two further crystallizations from 95% ethyl alcohol: m.p. 93.9–95.1°; $[\alpha]^{25}D$ −15°; infrared bands at 2.78, 3.31, 5.69, 14.87, and 15.01 (sh) μ.

Anal. Calcd. for $C_{29}H_{45}Cl_3O_3$: C, 63.55; H, 8.28; Cl, 19.41. Found: C, 63.43; H, 8.41; Cl, 19.46.

5α,6α-Epoxy-2-cholestene (6). A. From 6β-Benzoyloxy-2-cholesten-5α-ol.—To a solution of 6β-benzoyloxy-2-cholesten-5α-ol (2.134 g., 4.21 mmoles) in 75 ml. of methanola nd 25 ml. of water was added potassium hydroxide pellets (500 mg.). The solution was refluxed for 15.5 hr., cooled, diluted with 300 ml.

(15) We are indebted to Professor E. L. Wagner and Mr. J. E. Kent for this measurement on a Beckman IR-4 instrument.

(16) (a) P. v. R. Schleyer, D. S. Trifan, and R. Bacskai, *J. Am. Chem. Soc.*, **80**, 6691 (1958); (b) M. Oki and H. Iwamura, *Bull. Chem. Soc. Japan*, **32**, 306 (1959), and subsequent papers in this series; (c) for a review, see M. Tichy, *Chem. Listy*, **54**, 506 (1960).

(17) L. P. Kuhn, P. v. R. Schleyer, W. F. Battinger, Jr., and L. Eberson, *J. Am. Chem. Soc.*, **86**, 650 (1964).

(18) All melting points were taken on a calibrated Fisher-Johns block and are corrected. Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were obtained on 10% solutions in carbon tetrachloride except where otherwise noted. Optical rotations were observed on 2% chloroform solutions except where otherwise noted and are accurate to ±2°. We are indebted to Mr. Paul Bishop and Mr. Andrew Held for carrying out some of the large-scale preparations.

(19) L. F. Fieser and S. Rajagopalan, *J. Am. Chem. Soc.*, **71**, 3938 (1949).

(20) The double melting point behavior has been observed previously: ref. 2b and 4.

of water, and extracted with three 100-ml. portions of ether. The ether extracts were washed with two 100-ml. portions of water and dried over sodium sulfate. Evaporation yielded an oil which partially crystallized upon seeding with 2-cholestene-5α,6β-diol. Two crystallizations from methylcyclohexane afforded 2-cholestene-5α,6β-diol (870 mg., 2.16 mmoles), m.p. 133.1–133.9°, identified by comparison of infrared spectra. The methylcyclohexane mother liquors were evaporated and the residue was chromatograhed on 50 g. of Merck acid-washed alumina. The fractions eluted by hexane–benzene (4:1) were combined and crystallized from absolute ethyl alcohol to afford 323 mg. of white crystals, m.p. 74.8–76.0°. The analytical sample was prepared by two further crystallizations from ethyl alcohol: m.p. 74.8–75.9°, infrared bands at 3.30 and 15.21 μ.

Anal. Calcd. for $C_{27}H_{44}O$: C, 84.31; H, 11.53. Found: C, 84.15; H, 11.72.

B. From 6β-Trichloroacetoxy-2-cholesten-5α-ol.—A suspension of 6β-trichloroacetoxy-2-cholesten-5α-ol (2.4 g., 4.1 mmoles) and sodium methoxide (270 mg., 50 mmoles) in 50 ml. of methanol was refluxed for 15.5 hr. The hot solution was diluted with water to the cloud point, cooled, and seeded. The solid which separated was dried and chromatographed on 50 g. of alumina. Elution with hexane–benzene (1:2) afforded 1.2 g. of crystalline **6**, m.p. 75.1–76.1°. Further elution of the column with ether–benzene (1:4) afforded 63 mg. of **3**, identified by its infrared spectrum.

Acid Hydrolysis of 5α,6α-Epoxy-2-cholestene (6).—A solution of **6** (102 mg., 0.26 mmole) in 3 ml. of acetone was heated to boiling. Paraperiodic acid (65 mg.) dissolved in 1 ml. of water was added and the mixture was refluxed for 30 min. The mixture was cooled in an ice bath and the crystalline solid was collected. After one crystallization from hexane it showed m.p. and m.m.p. (with **3**) 133.1–133.9°. The infrared spectrum was superimposable on that of **3**.

6β-Chloro-2-cholesten-5α-ol (7).—A brisk stream of dry hydrogen chloride was passed through a solution of 5α,6α-epoxy-2-cholestene (317 mg., 0.83 mmole) in 7 ml. of chloroform for 30 min. The solution was then washed with 20 ml. of 5% aqueous sodium bicarbonate and dried over sodium sulfate. The solvent was evaporated and the residual oil was crystallized by trituration with ethanol. One crystallization from aqueous ethanol afforded 320 mg. (91%), m.p. 74.8–76.8°. The analytical sample was prepared by two further crystallizations from aqueous ethanol: m.p. 76.1–76.8°; infrared bands at 2.78, 3.31, 15.00 (sh), and 15.15 μ.

Anal. Calcd. for $C_{27}H_{45}ClO$: C, 77.01; H, 10.78; Cl, 8.42. Found: C, 76.84; H, 10.72; Cl, 8.18.

2,6-Dichlorobenzoic Acid.—Technical (90% by g.c.) 2,6-dichlorobenzal chloride (99.6 g.) was treated with concentrated sulfuric acid (150 ml.) according to the procedure of Stork and White[21] and maintained at 90–97° for 20 min. The cooled reaction mixture was poured over *ca.* 320 g. of ice. The lumps of crude 2,6-dichlorobenzaldehyde were broken up, and the entire slurry was warmed to 85° with stirring. Potassium dichromate (38.26 g.) was added during 1 hr. at such a rate as to maintain the temperature at 85–87°. The reaction mixture was stirred an additional 30 min. and then cooled in an ice bath. The green solid was collected, stirred with 5% sulfuric acid for 1 hr., and washed with water until the washings were no longer green. The solid was then dissolved in ether (*ca.* 600 ml.) and the ether solution was extracted with 1 l. of 5% sodium bicarbonate. The sodium bicarbonate solution was then filtered through Celite and the filtrate was warmed to expel ether, acidified with concentrated hydrochloric acid, and extracted with 500 ml. of methylene chloride. The methylene chloride solution was dried and filtered, and the solvent was evaporated. The remaining light yellow solid was crystallized from benzene yielding 29.36 g. (39%) of white crystalline 2,6-dichlorobenzoic acid, m.p. 142–144° (lit.[21] m.p. 143–144°). A portion of this material was converted to 2,6-dichlorobenzoyl chloride by the procedure of Stork and White,[21] b.p. 127–128° (19 mm.) [lit.[21] b.p. 110.5–111.5° (7.5 mm.)].

Attempted Esterification of 2-Cholestene-5α,6β-diol with 2,6-Dichlorobenzoyl Chloride. A.—A solution of 2-cholestene-5α,6β-diol (**3**, 402 mg., 1.00 mmole) and 2,6-dichlorobenzoyl chloride (221 mg., 1.1 mmoles) in 5 ml. of pyridine was refluxed for 13 hr. The cooled reaction mixture was worked up in the same way as in the preparation of **5a** and **5b** and gave 333 mg. of brown solid whose infrared spectrum was essentially unaltered from that of **3**.

B.—A solution of 2-cholestene-5α,6β-diol (**3**, 688 mg., 1.7 mmoles) in 25 ml. of benzene was boiled to expel water and then sodium hydride (100 mg., 4.16 mmoles) was added. The mixture was stirred and refluxed for 20 hr. when 355 mg. of 2,6-dichlorobenzoyl chloride was added. The mixture was stirred and refluxed for 5 hr., cooled, and washed with water, and the benzene was evaporated. The semicrystalline residue exhibited an infrared spectrum which was a composite of the infrared spectra of the diol **3** and the acid chloride.

6β-(2,6-Dichlorobenzoyloxy)-2-cholesten-5α-ol (7).—A solution of 5α,6α-epoxy-2-cholestene (384 mg., 1.00 mmole) and 2,6-dichlorobenzoic acid (191 mg., 1.00 mmole) in 10 ml. of dry benzene was refluxed for 11.5 hr. The benzene was evaporated under reduced pressure. The residual sirup crystallized upon the addition of a few drops of acetone. One crystallization from absolute ethanol afforded 407 mg. (71%), m.p. 139.1–140.0°. The analytical sample was prepared by a further crystallization from ethanol: m.p. 139.1–140.2°; $[\alpha]^{22}D$ +24°; infrared bands at 2.78, 3.31, 5.75, and 15.02 μ; $\lambda_{max}^{cyclohexane}$ 203 mμ (ε 42,000), 272 (340), and 279 (380) [lit.,[22] for 2,6-dichlorobenzoic acid, λ_{max}^{EtOH} 204 mμ (ε 28,000), 264 (435), and 274 mμ (500)].

Anal. Calcd. for $C_{36}H_{48}Cl_2O_3$: C, 70.94; H, 8.41; Cl, 12.32. Found: C, 70.82; H, 8.47; Cl, 12.40.

6β-(2,6-Dichlorobenzoyloxy)-2,4-cholestadiene (1).—To a solution of 6β-(2,6-dichlorobenzoyloxy)-2-cholesten-5α-ol (635 mg., 1.1 mmoles) in 25 ml. of dry pyridine cooled in an ice bath was added 0.5 ml. of thionyl chloride. After 5 min., 5 ml. of water was added slowly, followed by about 10 g. of cracked ice. The gummy precipitate was collected, dried to constant weight at 0.1 mm., and dissolved in 20 ml. of methylene chloride. The methylene chloride solution was filtered slowly through 1 g. of decolorizing carbon and the carbon was washed with about 10 ml. of methylene chloride. The combined filtrate and washings were evaporated and the residue was dried to constant weight at 0.1 mm., yielding 450 mg. (74%) of white foamy solid: $\lambda_{max}^{cyclohexane}$ 267 mμ (ε 5100) and 203 mμ (ε 49,500); $[\alpha]^{20}D$ +114 ± 1° (*c* 2, $CHCl_3$); infrared bands at 3.29, 5.79, 13.70, and 14.35 μ.

Anal. Calcd. for $C_{34}H_{46}Cl_2O_2$: C, 73.23; H, 8.31; Cl, 12.72. Found: C, 72.97; H, 8.30; Cl, 12.72.

(21) G. Stork and W. N. White, *J. Am. Chem. Soc.*, **78**, 4609 (1956).

(22) C. M. Moser and A. I. Kohlenberg, *J. Chem. Soc.*, 804 (1951).