from a reaction mixture tenfold in phenol is enhanced considerably at the expense of diamino ether formation. These results are summarized in Table I.

Experimental[10]

The amino ethers and diamino ethers for which physical constants and derivatives are listed in Table II were prepared in a manner analogous to that described in method A for β-aminobutyl phenyl ether and β-(β-aminobutyl)-aminobutyl phenyl ether, respectively. The derivatives were prepared by standard procedures.

β-Aminobutyl Phenyl Ether. Method A.—To a solution of 40 g. (0.42 mole) of reagent grade phenol in 200 ml. of refluxing chloroform, 10 g. (0.14 mole) of 2-ethylethylenimine in 50 ml. of chloroform was added dropwise over a half-hour period while the solution was stirred mechanically. Refluxing was continued for three hours. The chloroform was distilled at atmospheric pressure and the remainder was subjected to fractional distillation from a modified Claisen flask. After removing the unreacted phenol, the following fractions were collected: b.p. 80–105° (5 mm.), 105–118° (5 mm.) and 118–145° (5 mm.). From the second fraction, another distillation gave 8.0 g., b.p. 108–113° (5 mm.), of a colorless liquid with an amine odor which contained traces of phenol. A constant index of refraction could not be obtained by repeated distillation. The sample was dissolved in excess 5% hydrochloric acid and extracted with 100 ml. of ether in three portions. The acid solution was then made slightly alkaline with 5% sodium hydroxide and the free amino ether extracted with ether. Distillation at reduced pressure in a nitrogen atmosphere gave a sample of analytical purity which was used for the density and index of refraction measurements; yield 7.0 g., 30%, b.p. 74–77° (0.9 mm.).

Method B.—A Gabriel synthesis of β-aminobutyl phenyl ether following the procedure of Cope, *et al.*,[11] as used by Meguerian[4] on the sulfur analog established the structure of the product of b.p. 74–77° (0.9 mm.) just described. Over-all yield in the four reactions was 4%. The phenylthiourea of the product from the Gabriel synthesis resulted in a m.p. 112–114° and the mixed m.p. with the phenylthiourea from IIIb, m.p. 113–113.5°, gave no depression.

β-(β-Aminobutyl)-aminobutyl Phenyl Ether. Method A.—The third fraction, b.p. 118–145° (5 mm.), from the reaction (preceding paragraph) of 2-ethylethylenimine and phenol was redistilled, b.p. 142–151° (3 mm.), yield 5.6 g., from which 5.0 g., 30%, of pure β-(β-aminobutyl)-aminobutyl phenyl ether was obtained using the same method of purification as described for β-aminobutyl phenyl ether.

Method B.—One and one-tenth grams of 2-ethylethylenimine was sealed in a glass tube with 7.6 g. of β-aminobutyl phenyl ether and 0.2 g. of ammonium chloride.[3] After 44 hours in an oil-bath at 100°, a fraction, b.p. 117–120° (0.8 mm.), $n^{25}D$ 1.5053, was obtained; yield 1.0 g., 27.4%. A polymer was formed to the extent of 45.4% and 25% of unreacted imine was recovered. The benzamide of this compound, recrystallized from chloroform and petroleum ether (b.p. 60–68°) gave a m.p. 198–200°. The mixed m.p. with the benzamide from the product in method A gave no depression.

A Diethylpiperazine.[12]—The forerun of the distillation of the β-aminobutyl phenyl ether, b.p. 80–105° (5 mm.), crystallized on cooling and was found to contain 0.4 g. of a molecular compound of phenol and a piperazine, presumably 2,5-diethylpiperazine. The compound was recrystallized from petroleum ether (b.p. 60–68°), m.p. 72–73.5°. Since the analysis did not distinguish the molecular compound, $C_{20}H_{30}N_2O_2$, from the amino ether, $C_{10}H_{15}NO$, the phenylthiourea and oxalate derivatives were prepared directly from the molecular compound. The phenylthiourea was recrystallized from a large volume of absolute methanol and sublimed above 200° (0.06 mm.); m.p., closed tube, 244–246° dec.

Anal. Calcd. for $C_{22}H_{28}N_4S_2$: C, 64.04; H, 6.84. Found: C, 64.00; H, 6.82.

The oxalate was recrystallized from water and sublimed above 200° (0.06 mm.); m.p. 300–301° (dec.) in closed tube. The piperazine previously reported[3] gave the same oxalate, m.p. 298–301° dec.

Anal. Calcd. for $C_{10}H_{20}N_2O_4$: C, 51.71; H, 8.68. Found: C, 51.87; H, 8.65.

Acknowledgment.—Most of the work described was done at the University of Wisconsin during a leave of absence. I appreciate the kindness of the Organic Chemistry Department in extending the facilities of their laboratories to me for this work. Most of the analyses were performed there by Messrs. B. G. Buell and E. A. Shiner.

(10) All m.p.'s are corrected; b.p.'s are uncorrected.

(11) A. C. Cope, H. R. Nace, W. R. Hatchard, W. H. Jones, M. A. Stahlmann and R. B. Turner, THIS JOURNAL, **71**, 554 (1949).

(12) No evidence for the formation of a piperazine in reactions involving 2,2-dimethylethylenimine was obtained.

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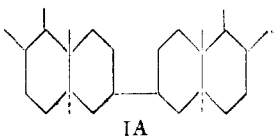
[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, FACKENTHAL LABORATORIES OF FRANKLIN AND MARSHALL COLLEGE]

Bisteroids. I. Bicholestanyl. The Structure of Bicholesteryl and 3,3′-Bis-3,5-cholestadiene[1]

BY EDWARD N. SQUIRE

Three methods for the preparation of bicholestanyl (X) are described and the preparation of cholestanylmagnesium chloride is reported for the first time. Evidence is presented which confirms the appointed structures of bicholesteryl and 3,3′-bis-3,5-cholestadiene. Comparisons of the specific and molecular rotations of several steroids and their bisteroid derivatives are demonstrated and the ultraviolet absorption spectra of 3,3′-bis-3,5-cholestadiene in ether and alcohol solvents are illustrated.

The preparation of steroid hydrocarbons with the general structure shown in IA and with a variety of groups at C_{17} was undertaken with the aim of studying their physical and physiological properties.[2] To this end bicholestanyl (X) was prepared as a means of determining the most effective synthetic route to the desired compound. Five avenues of approach were apparent. (1) The formation of cholestenone pinacol followed by dehydration[3] and hydrogenation. The dehydration has been described by Windaus, who employed

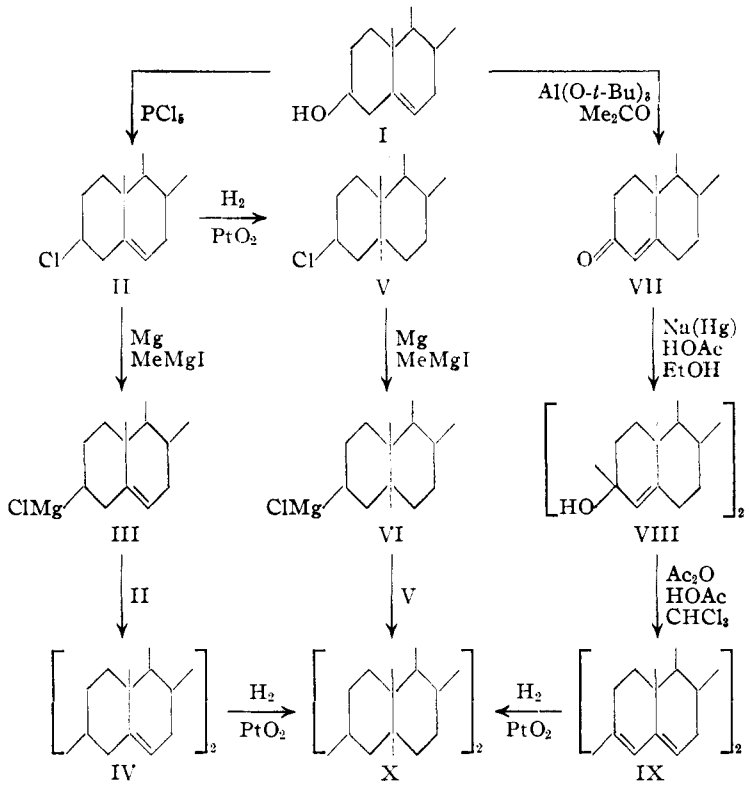


IA

(1) Presented at the Philadelphia Meeting of the American Chemical Society, April, 1950.

(2) E. N. Squire and E. W. Squire, unpublished results, have found in feeding experiments with 3–4 months old male hamsters that 55% of the orally administered bicholesteryl (IV) is not excreted. Feeding experiments using the saturated hydrocarbon, bicholestanyl (X), were therefore of interest.

(3) A. Windaus, *Ber.*, **39**, 521 (1906).



acetic anhydride in refluxing chloroform. Butenandt[4] has likewise effected dehydration of VIII employing chloroform solutions of the pinacol exposed to sunlight; the dehydration was presumably due to the catalytic action of hydrogen chloride formed upon the decomposition of the chloroform. The yields were low. (2) The coupling of the cholesteryl Grignard reagent[5] (III) and subsequent hydrogenation. (3) The coupling of the cholestanyl Grignard reagent (VI). (4) The hydrogenolysis and hydrogenation of cholestenone pinacol (VIII).[6] Although this approach appeared feasible, the yield of the hydrogenolysis product, $C_{54}H_{90}$, was discouraging and the identity of the product was doubtful. (5) Dehydration of cholestanone pinacol and hydrogenation of the resulting diene. Attempts were made to prepare this pinacol but treatment of cholestanone with sodium amalgam in ethanol–acetic acid solutions or with zinc amalgam in acetic acid–ethanol or hydrochloric acid–ethanol solutions failed to produce the pinacol.

The first three synthetic approaches to bicholestanyl (X), I → IV, II → VI and VII → IX, were successfully accomplished. A comparison of these three preparative methods indicated that the coupling of the cholesterylmagnesium chloride followed by the hydrogenation of IV gave the greater over-all yield, 8%. Furthermore, the hydrogenation of bicholesteryl (IV) and 3,3′-bis-3,5-cholestadiene (IX) to yield bicholestanyl (X) afforded further verification for the appointed structures of each. Specifically, the C_3–$C_{3'}$ bond in each was proven, since bicholestanyl (X) was also formed by the coupling of cholestanylmagnesium chloride (VI).

Although it had been shown that bicholesteryl does not possess the *i*-steroid structure[7] in either part of the molecule, the positive optical rotation $[\alpha]_D$ +5° (chloroform), +30° (benzene)[8] was apparently anomalous. This is borne out in Table I and the comparison of cholestane and bicholestanyl demonstrates a negative rotatory effect upon formation of the bisteroid; on the other hand, the joining of two 5-cholestenyl groups at C_3, $C_{3'}$ results in a positive rotational increment as in the transformation of 5-cholestene to bicholesteryl. Another comparison, not quite analogous, demonstrates a positive increment in the conversion of cholestenone to cholestenone pinacol. In these cases just cited, the C_3 atoms of the bisteroid are asymmetric. When C_3 and $C_{3'}$ are not rotophores as in the transformation of 3,5-cholestadiene to 3,3′-bis-3,5-cholestadiene, there occurs an enhancement of the negative specific rotation.

Whereas the concentrations of the bisteroids whose optical rotations are reported in Table I are comparable, the concentrations for the other steroids whose specific rotations are cited in the literature are not equal to those of the bisteroids and therefore absolute comparisons of specific or molecular rotation changes cannot be made. Furthermore, the configurations at C_3 and $C_{3'}$ in the bisteroid molecules are unknown. However, it is interesting to note that the transformation from the steroid to bisteroid derivative is accompanied by a molecular rotation change approximately equal to an integral multiple of 41°, *e.g.*, 5-cholestene-bicholesteryl; $\Delta M_D = 244° \cong 6 \times 41°$. Cholestenone-cholestenone pinacol $\Delta M_D = 452° \cong 11 \times 41°$, etc.

TABLE I

Steroid	$[\alpha]_D$ (chloroform)	M_D
Cholestane[8]	23	86
Bicholestanyl	0	0
5-Cholestene[9]	−56	−207
Bicholesteryl	5 (30, benzene)[8]	37
3,5-Cholestadiene[10]	−129	−475
3,3′-Bis-3,5-cholestadiene	−260	−1911
Cholestenone[11]	89	342
Cholestenone pinacol[4]	103	794

As to the structure of cholestenone pinacol (VIII) Butenandt[12] has supplied evidence to refute the formulation suggested by Bergmann and Hirschberg[13] but the pinacol structure[14] and evi-

(4) A. Butenandt and L. Poschmann, *Ber.*, **73B**, 893 (1940).
(5) R. H. Baker and E. N. Squire, THIS JOURNAL, **70**, 1487 (1948).
(6) F. Galinovsky and H. Bretschneider, *Monatsh.*, **72**, 190 (1938).
(7) R. H. Baker and E. N. Squire, THIS JOURNAL, **70**, 4134 (1948).
(8) H. E. Stavely and W. Bergmann, *J. Org. Chem.*, **1**, 567 (1937).
(9) F. Mauther, *Monatsh.*, **28**, 1113 (1907).
(10) F. S. Spring and G. Swain, *J. Chem. Soc.*, 83 (1941).
(11) L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, N. Y., 1949, p. 262.
(12) A. Butenandt and A. Wolff, *Ber.*, **72B**, 1121 (1939).
(13) E. Bergmann and Y. Hirschberg, *Nature*, **142**, 1037 (1938).
(14) W. H. Strain, in "Organic Chemistry," Henry Gilman, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 1388.

dence for the tetraene structure (IX) were open to question.

Butenandt[4] has based the structure of the tetraene upon the analogous properties of 3,5-cholestadiene reported by Stavely.[8] It is known that the 2,4-diene is reduced whereas the 3,5-diene is not affected by treatment with sodium in amyl alcohol.[8,15] We have attempted reduction of IX in a variety of alcohols over platinum oxide catalyst at three to four atmospheres of hydrogen for 18 hours with vigorous shaking; most of the finely powdered tetraene remained suspended. Only after filtering off the catalyst and almost all of the starting material could a small amount (less than 10%) of the reduced product X and its epimers be secured. Because of the extremely slight solubility of IX in alcohols (and ether), the reduction of the tetraene by sodium in alcohol would not be expected to furnish sufficient evidence to distinguish between structures with unsaturation at 2,4,2′, 4′- and 3,5,3′,5′-. Furthermore, if IX were a 2,4,2′,4′-tetraene it would presumably exhibit both the properties of homoannular and heteroannular dienes.

It is well known that the catalytic hydrogenation of 2,4-cholestadiene in neutral media yields coprostane[15] whereas reduction of the 3,5-diene or 5-cholestene in neutral media gives cholestane[8] as the principal product. The catalytic hydrogenation of 3,3′-bis-3,5-cholestadiene in neutral media resulted in a 10 per cent. yield of bicholestanyl (X) identical with that prepared from the cholestanylmagnesium chloride reagent (VI). The low yield of an identical bicholestanyl was undoubtedly due to the formation of epimers through hydrogenation at C_3 and $C_{3'}$; because of this low yield it was impossible to absolutely verify the structure of the tetraene by hydrogenation procedures. However, the isolation of bicholestanyl from the hydrogenation products did indicate the 3,5,3′,5′-tetraene structure. Likewise, the hydrogenation of bicholesteryl (IV) afforded a 70% yield of the same hydrocarbon (X), $C_{54}H_{94}$, m.p. >300° with decomposition starting at 265°, $[\alpha]_D$ 0°.

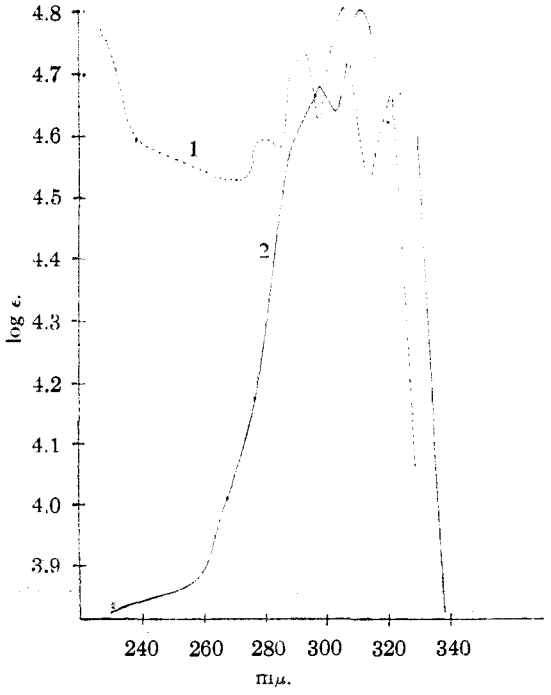


Fig. 1.—Ultraviolet absorption spectra of 3,3′-bis-3,5-cholestadiene: 1, ether solvent; 2, chloroform solvent.

To further substantiate the orientation of the double bonds in the tetraene, the ultraviolet absorption spectrum of this compound which was first studied by Butenandt[4] was re-examined. Figure 1 illustrates the absorption spectra in ether and chloroform. In ether the absorption spectrum maxima are at 293, 305 and 321 mμ with log ε values of 4.73, 4.80 and 4.66, respectively. In chloroform the maxima are shifted slightly to higher wave lengths at 298, 312 and 323 mμ with log ε values of 4.68, 4.80 and 4.67, respectively. Compounds which contain a —C=C—C=C—C=C—C=C— chromophore group show maximum absorption at about 290 mμ and with approximate log ε values of 4.8.[16] These approximations are in accord with absorption maxima at 293 and 298 mμ in ether and chloroform, log ε 4.73, 4.68, respectively. Furthermore, it is known that the addition of each —C=C— group to a conjugated diene grouping will shift the absorption maxima approximately 30 mμ in the direction of higher wave lengths. 3,5-Cholestadiene exhibits an absorption spectrum with maxima at 229, 235 and 244 mμ.[17] The addition of two double bonds to this system with a resultant 3,3′-bis-3,5-cholestadiene structure would shift the maxima approximately to 289, 295 and 304 mμ. Two of the absorption maxima exhibited by the tetraene do occur at wave lengths within 2 mμ of these estimated values.

Syntheses starting with cholesterol (I) are diagrammed. At this time the other products arising from the catalytic hydrogenation of the tetraene (IX) are being investigated.

Acknowledgment.—This project was carried out with the financial assistance of the Research Corporation, New York.

Experimental[18]

Cholesteryl Chloride (II).—This was prepared as previously described[5] and from 100 g. of cholesterol there was obtained 76 g. of cholesteryl chloride, m.p. 94–95°, $[\alpha]^{25}D$ −27° (170 mg. made up to 5.00 ml. with chloroform, α −0.45°, *l*, 0.5 dm.), lit., m.p. 96–97°,[5] $[\alpha]_D$ −26.[19]

Bicholesteryl (III).—The cholesteryl Grignard reagent was prepared in the usual manner from 5.0 g. of cholesteryl chloride.[5] The total reflux time for the formation of this reagent was 47 hours. Then the mixture was cooled and stirred under 850 mm. of carbon dioxide for 32 hours. Following hydrolysis the entire product(s) were extracted with benzene, dried, filtered and evaporated to dryness. The separation of the bicholesteryl from the carboxylic acid was difficult, due to similar solubilities; alkaline extraction of ether or benzene solutions containing the two

(15) H. E. Stavely and W. Bergmann, *J. Org. Chem.*, **1**, 575 (1937).

(16) G. R. Harrison, R. C. Lord and J. R. Loofbourow, "Practical Spectroscopy," Prentice-Hall, Inc., New York, N. Y., 1948, p. 275.

(17) W. H. Strain, in "Organic Chemistry," Henry Gilman, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 1395.

(18) Microanalyses by Dr. Carl Tiedcke.

(19) L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, N. Y., 1949, p. 259.

was tedious, due to the formation of emulsions and to the slight solubility of the carboxylic acid salt in aqueous media. Therefore, the following method of separation was evolved in which the carboxylic acid was converted to a very soluble derivative and the bicholesteryl separated on the basis of low solubility.

To 1.30 g. of the crude products of the Grignard reagent there was added 50 ml. of anhydrous 2-butanol and 20 drops of concentrated sulfuric acid; the mixture was heated at reflux temperature under anhydrous conditions for five hours.[20] During this time the bicholesteryl remained suspended. After cooling, the solution was poured into 200 ml. of distilled water containing 41.8 milliequivalents of sodium carbonate. The mixture was transferred to a separatory funnel and 200 ml. of ether added. The aqueous layer was withdrawn and the ether-*s*-butyl alcohol mixture washed four times with 50-ml. portions of distilled water. Crystallization from the ether–alcohol mixture afforded 195 mg. (15.2% of the theoretical yield) of bicholesteryl, m.p. 266–269°, $[\alpha]^{25}D$ +5° (21.8 mg. made up to 5.00 ml. with chloroform, α +0.10°, *l*, 0.5 dm.); lit.[5] m.p. 271–272°, $[\alpha]^{25}D$ +30° (5.0 mg. made up to 5.00 ml. with benzene, α +0.05°, *l*, 2 dm.).

Cholestanyl Chloride (V).—This preparation was carried out according to a modification of Marker's method.[21] To a mixture containing 15 ml. of ethanol and 15 ml. of ethyl ether contained in a 50-ml. erlenmeyer flask was added 0.63 g. of cholesteryl chloride and 38 mg. of platinum oxide catalyst.[22]

This was subjected to 2 atm. of hydrogen for one hour with vigorous stirring; filtration followed by evaporation to about 10 ml. gave 0.51 g. of the chloride as colorless crystals, m.p. 115–115.5°, $[\alpha]^{24}D$ +28° (61.2 mg. made up to 5.00 ml. with chloroform, α +0.17°, *l* 0.5 dm.), lit. m.p. 112°,[21] 115,[23] $[\alpha]D$ +27°.[23]

Cholestenone (VII).—This was prepared according to the method of Oppenauer[24] and petroleum ether solutions of the crude product were chromatographed on alumina prior to crystallization from petroleum ether–methanol mixtures. Thus 20 g. of cholesterol gave 17.9 g. (90%) of cholestenone, m.p. 78–79°, $[\alpha]^{25}D$ +90.5° (127.0 mg. made up to 5.00 ml. with chloroform, α +1.15°; *l*, 0.5 dm.); lit.[11] m.p. 82°, $[\alpha]D$ 89°.

Cholestenone Pinacol (VIII).—A slight modification of the method employed by Windaus[3] gave better yields. To 2.0 g. of cholestenone contained in 150 ml. of a 1:1 mixture of propanol and acetic acid, there was added over a period of one-half hour 300 g. of 2% sodium amalgam; during the last five minutes of the addition the solution was boiling. It was then poured into 600 ml. of distilled water and the product, a white solid, separated to the top. This was filtered off at the pump, washed with distilled water and dried. The crude pinacol was then taken up in 100 ml. of hot benzene, filtered, and evaporated to about 25 ml.; crystals started to form upon cooling and 100 ml. of hot acetone was added. Upon standing overnight beautiful colorless crystals separated out. Filtration followed by evaporation and crystallization from the mother liquor gave the pinacol, m.p. 193–203°. Recrystallization of this fraction from acetone–benzene mixtures afforded 1.7 g. (85%) of cholestenone pinacol, m.p. 200–205°, $[\alpha]^{25}D$ +110° (20.0 mg. made up to 5.00 ml. with chloroform, α +0.22°; *l*, 0.5 dm.), lit.[4] m.p. 200° *ca.*, $[\alpha]^{21}D$ +103°.

In addition to this product there was isolated about 0.1 g. of an unidentified solid, m.p. 237–240°.

3,3′-Bis-3,5-cholestadiene (IX).—Windaus'[3] method was modified to include acetic acid in the dehydration which apparently hastened the reaction. Thus, 3.0 g. of cholestenone pinacol was taken up in 250 ml. of chloroform and at reflux temperature 5 ml. of acetic anhydride and 5 ml. of glacial acetic acid were added. The refluxing was continued for four hours and then the chloroform was slowly distilled over another four-hour period. One hundred milliliters of hot methanol was added to the acetic-acid–acetic-anhydride mixture. After cooling, the solution was filtered to afford a light yellow solid, m.p. 232–245°. Recrystallizations from chloroform–acetone mixtures gave 2.6 g. (83%) of the tetraene as light yellow, shiny crystals, m.p. 243–247° dec., $[\alpha]D^{25}$ −260° (25.5 mg. made up to 10.00 ml. with chloroform, α −0.33°; *l*, 0.5 dm.), lit.[4] m.p. 244–246°, $[\alpha]^{21}D$ −230°.

Evaporation of the solvent from the above reaction yielded a small amount of unidentifiable amorphous material.

Bicholestanyl (X) Method 1.—The hydrogenation of 3,3′-bis-3,5-cholestadiene. One hundred milligrams of the finely divided tetraene (IX) and 100 mg. of platinum oxide catalyst[22] were suspended in 250 ml. of cyclohexane and subjected to 3 atm. of hydrogen for 18 hours with vigorous agitation. The end-point in the reduction was conveniently noted by the disappearance of the yellow color in the solution. After filtration, the solution was evaporated to dryness to yield 98 mg. of the steroid hydrocarbon, m.p. *ca.* 270 to 300°. Crystallizations of this from chloroform and chloroform–cyclohexane mixtures yielded a relatively insoluble chloroform fraction (60 mg.) and a chloroform soluble fraction (10 mg.). This latter fraction commences to decompose about 265–270°; m.p. >300°, $[\alpha]^{25}D$ 0° (15 mg. made up to 5.00 ml. with chloroform, α 0.00°; *l*, 0.5 dm.).

Anal. Calcd. for $C_{54}H_{94}$: C, 87.26; H, 12.74. Found: C, 87.29; H, 12.43; C, 87.42; H, 12.30.

Method 2. The Hydrogenation of Bicholesteryl.—Similar reduction of 100 mg. of the diene (IV) under 3 atm. of hydrogen gave the same beautiful, fine needles after filtering and evaporating the solvent; the product, 97 mg., m.p. 242–300°, was crystallized from chloroform and cyclohexane–chloroform mixtures to yield 70 mg. of bicholestanyl, decomposition at 265–270° and m.p. >300°, $[\alpha]^{25}D$ 0° (21.7 mg. made up to 5.00 ml. with chloroform, α 0°, *l*, 0.5 dm.). There was no depression in the decomposition point when this sample was mixed with X produced from the tetraene (IX). Mixtures of either sample of bicholestanyl with bicholesteryl, m.p. 266–269°, produced melting starting at 240° with softening at 227°. Bicholestanyl (X) did not react with bromine in chloroform solutions.

Anal. Calcd. for $C_{54}H_{94}$: C, 87.26; H, 12.74. Found: C, 87.28, 87.40; H, 12.09, 12.25.

Method 3. The Coupling of Cholestanylmagnesium Chloride (VI).—Methylmagnesium iodide was prepared in the usual manner from 1.0 ml. of methyl iodide, 1.0 g. of magnesium powder and 5 ml. of dry ether contained in a 50-ml. round-bottom flask equipped with a reflux condenser and in a nitrogen atmosphere. To this mixture was added 0.82 g. of cholestanyl chloride in 15 ml. of absolute ether. The reaction mixture was then heated at reflux temperature for 22 hours, then cooled to 0° and treated with carbon dioxide gas at 1.5 atm. pressure for 18 hours. The contents of the flask were then poured onto 100 g. of ice in 20 ml. of concentrated hydrochloric acid. After standing 3 hours the mixture was transferred to the separatory funnel and extracted with 100 ml. of ether; following this, the ether layer was extracted with five 20-ml. portions of 0.1 *N* sodium hydroxide and finally with five 10-ml. portions of distilled water. The ether layer was then dried over anhydrous sodium sulfate, filtered and evaporated to dryness, yielding a white solid which, when recrystallized from ether, afforded 26 mg. (3.4%) of bicholestanyl, decomposition commenced at 265° and m.p. >300°, $[\alpha]^{25}D$ 0° (17.8 mg. made up to 5.00 ml. with chloroform, α 0°, *l*, 0.5 dm.). Mixtures of this compound with either of the other two samples of bicholestanyl did not produce a depression in the decomposition point and the mixed melting points were greater than 300°.

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(20) It is conceivable that the heating at reflux temperature in 2-butanol with sulfuric acid could have caused migration of the double bonds. This, however, does not occur, since the product of this reaction is identical with bicholesteryl previously prepared and not exposed to acid.[5]

(21) R. E. Marker, THIS JOURNAL, **57**, 1755 (1935); R. E. Marker, F. C. Whitmore and O. Kamm, *ibid.*, **57**, 2358 (1935).

(22) Prepared according to R. Adams, *ibid.*, **44**, 1397 (1922); **45**, 2171 (1923).

(23) L. F. Fieser and M. Fieser, "Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, N. Y., 1949, p. 259.

(24) R. V. Oppenauer, *Rec. trav. chim.*, **56**, 137 (1937).