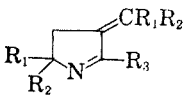
TABLE II



R_1	R_2	R_3	Formula	B.P., °C.	mm. Hg	$n_D^{t°}$	Picrate	Calculated, % C	Calculated, % H	Found, % C	Found, % H
CH_3	CH_3	2—$CH_3C_6H_4$	$C_{16}H_{21}N$	108–110	3	1.5370^{23}	146–148[a]	84.5	9.2	84.3	8.5
CH_3	CH_3	3—$CH_3C_6H_4$	$C_{16}H_{21}N$	120–121	1	1.4805^{20}	124–125[b]	84.5	9.2	84.2	8.8
CH_3	CH_3	4—$CH_3C_6H_4$	$C_{16}H_{21}N$	121–122	0.7	1.5399^{20}	136–138	84.5	9.2	83.2[c]	8.7
CH_3	CH_3	H	$C_9H_{15}N$	90–91	30	1.4835^{17}	148–150[d]	78.8	10.9	78.8	10.5
CH_3	CH_3	—$C(CH_3)$=CH_2	$C_{12}H_{19}N$	86–88	5	1.4905^{20}	149–150	81.4	10.7	80.9	10.2
CH_3	C_2H_5	H	$C_{11}H_{19}N$	74–75	3	1.4940^{20}	117–118[e]	80.0	11.5	79.8	11.0
CH_3	C_2H_5	CH_3	$C_{12}H_{21}N$	62–64	2	1.4780^{17}	[f]	80.4	11.7	80.1	11.5
CH_3	C_2H_5	—CH=CH_2	$C_{13}H_{21}N$	88–90	10	1.4857^{21}	[f]	81.5	10.9	81.1	10.6
CH_3	C_2H_5	—$C(CH_3)$=CH_2	$C_{14}H_{23}N$	107–108	18	1.4868^{17}	[f]	81.9	11.1	81.8	10.8

[a] From aqueous picric acid and the pyrroline hydrochloride. [b] Mixture with picric acid melted at 85–112°. [c] Performed in duplicate; second result C, 82.9; H, 8.8. [d] With decomposition. [e] Mixture with picric acid melted at 82–108°. [f] Does not form a picrate.

additional hour at which time it was poured over 300–400 g. of chipped ice. The aqueous solution was extracted several times with chloroform and then neutralized with 30% sodium hydroxide solution. The alkaline solution was extracted several times with ether and the ethereal layer was dried overnight with anhydrous potassium carbonate. The ether was removed by a steam bath and the residue containing the heterocyclic base was distilled *in vacuo*.

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NEW ORLEANS 22, LA.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Preparation and Solvolysis of Epi-ψ-cholesterol

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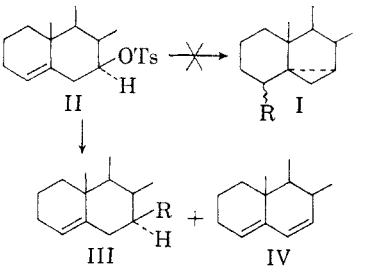
The preparation of cholest-4-en-7-one, epi-ψ-cholesterol, and epi-ψ-cholesteryl tosylate is discussed. Solvolysis of epi-ψ-cholesteryl tosylate under three different *i*-steroid-forming conditions afforded predominantly cholesta-4,6-diene with no evidence of a 5,7-cyclosteroid.

Recently Shoppee and co-workers[3,4] attempted to prepare a 5,7-cyclosteroid (I) by solvolyzing ψ-cholesteryl tosylate (cholest-4-en-7β-*p*-toluenesulfonate) (II), under a variety of *i*-steroid-forming conditions. In the reactions studied the major products were a 4,5 unsaturated, 7β-substituted steroid (III) (the 7 substituent depends upon the solvent used) and the conjugated diene, cholesta-4,6-diene (IV), with no observed ring B *i*-steroid formation. Also, an attempt by Shoppee[3] to prepare epi-ψ-cholesterol (cholest-4-en-7α-ol)



(XI), through the unknown cholest-4-en-7-one (X), proved to be unsuccessful.

In the present paper we would like to report the synthesis of cholest-4-en-7-one (X), epi-ψ-cholesterol (XI), epi-ψ-cholesteryl tosylate (XII), and the solvolysis of the latter under conditions in which *i*-steroids are known to be formed. The route used for the preparation of cholest-4-en-7-one (X) and epi-ψ-cholesterol (XI) may be seen below. Cholesteryl acetate (VI), by allylic oxidation with

(1) This article is based upon a dissertation by Gerald J. Kent in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University.

(2) General Electric Fellow 1957–58.

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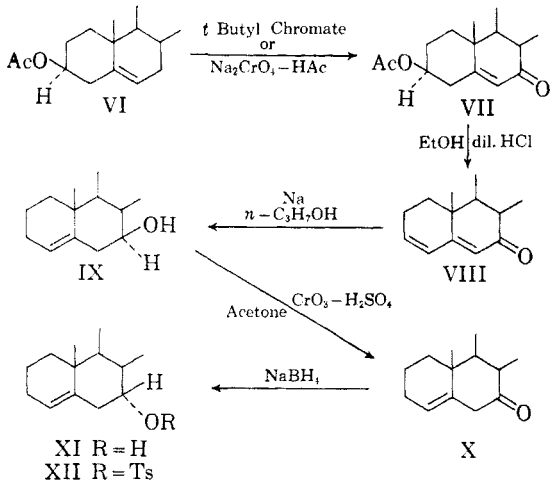
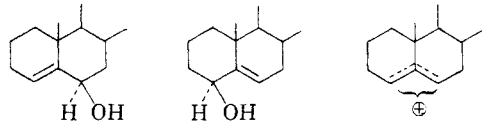


either tertiary butyl chromate[5–8] or sodium chromate–acetic acid[7,9] was converted in good yield to 7-keto-cholesteryl acetate (VII). Treatment of this unsaturated keto acetate with dilute hydrochloric acid in ethanol[10,11] gave a 77% yield of cholesta-3,5-dien-7-one (VIII) which was reduced by sodium in n-propanol[3,11,12] to ψ-cholesterol (IX) (64%). Using the standard chromium trioxide–sulfuric acid reagent developed by Jones *et al.*,[13] and extended by Djerassi and co-workers,[14] ψ-cholesterol was oxidized to the unknown β-γ unsaturated ketone cholest-4-en-7-one (X). The infrared spectrum of this material showed a strong carbonyl band at 5.84 μ (1712 cm.$^{-1}$) and the ultraviolet spectrum showed no appreciable absorption in the 200–300 mμ region. This was indicative of a nonconjugated keto function, but in order to establish unequivocally the structure as cholest-4-en-7-one (X), the 4,5 double bond was isomerized by heating in 10% methanolic potassium hydroxide followed by chromatography to give the known cholest-5-en-7-one (identical with an authentic sample prepared by allylic oxidation of cholest-5-ene). In order to prepare the thermodynamically less stable, 7α axial hydroxy isomer, cholest-4-en-7-one(X) was reduced with sodium borohydride.[6] A mixture of ψ-cholesterol (IX) and epi-ψ-cholesterol (XI) was obtained which, after chromatography on neutral alumina, gave 60% of the less stable isomer. Use of lithium aluminum hydride[6,15,16] instead of sodium borohydride in the reduction step gave a lower yield of the desired isomer. This is in agreement with the views expressed by Dauben and co-workers.[6,17] The structure of epi-ψ-cholesterol (XI) was assigned on the basis of mixed melting point (depression with ψ-cholesterol), infrared spectrum and oxidation with standard chromium trioxide–sulfuric acid reagent to the starting material cholest-4-en-7-one (X).

After the preparation of epi-ψ-cholesteryl tosylate was accomplished with some difficulty[16] by reaction in pyridine and p-toluenesulfonyl chloride[3,18] our attention turned to the solvolysis of this ester under *i*-steroid conditions. Treatment of the tosylate with potassium acetate–acetic acid resulted in a yellow oil which after chromatography on neutral alumina gave a white crystalline compound (73.4%). This was shown from melting point, optical rotation, infrared and ultraviolet spectra, and microanalysis to be identical to cholesta-4,6-diene[3,4,19] (IV).

Hydrolysis of epi-ψ-cholesteryl tosylate (XII) with potassium acetate–aqueous acetone mixture resulted in a colorless oil which was chromatographed on neutral alumina. Elution with pentane gave material (61.5%) which after recrystallization from acetone was shown from melting point, mixed melting point, optical rotation, and infrared and ultraviolet spectra to be identical with cholesta-4,6-diene (IV). Elution with benzene-ether (4:1) gave a product (5.4%) that melted at 85.2–87.1°,[4] and from infrared spectral, rotational, and analytical data was shown to be cholest-4-en-6β-ol (XIII).[20,21] Further elution with the same solvent system gave 9.5% of cholest-5-en-4β-ol (XIV)[20,21] whose structure was assigned on the basis of melting point, infrared spectrum, optical rotation, and analytical data. It is possible that these products are formed from an intermediate



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cationic species such as XV which has been described by Schmid and Kagi.[22]

Solvolysis of epi-ψ-cholesteryl tosylate with potassium acetate–acetic anhydride mixture gave a dark yellow solid which was chromatographed on neutral alumina. Pentane elution afforded a white crystalline solid (62%) identical in all respects to cholesta-4,6-diene (IV).

From the foregoing experimental data of the three solvolyses described, it may be concluded that an elimination reaction occurs in preference to transannular *i*-steroid formation. This result was not unexpected for in the analogous case of epicholesterol (cholest-5-en-3α-ol)[20,22–24] the conjugated diene, cholesta-3,5-diene, is preferentially formed. In this study no 5,7-cyclosteroid formation has been observed.

EXPERIMENTAL[25]

7-Keto cholesteryl acetate (VII). (*A*) *Tertiary butyl chromate method.*[8] Tertiary butyl chromate was prepared in the following manner. To 235 ml. of purified tertiary butyl alcohol was added 93 g. of chromic anhydride in "small portions" (as a precaution it is best to do this reaction behind a safety shield and care should be taken not to permit the chromic anhydride to cake at the mouth of the flask). During the addition the reaction mixture was maintained at 30–40° with the aid of an ice bath. Addition took about 1 hr., after which the reaction mixture was stirred for an additional 15 min. The mixture was then transferred to a separatory funnel and extracted with 650 ml. of dry carbon tetrachloride. The organic layer was dried over anhydrous sodium sulfate, filtered, and the inorganic drying agent was washed with 400 ml. of dry carbon tetrachloride. The organic mixture was concentrated under reduced pressure in a water bath at 45–50° to a volume of 500 ml. To ensure that the excess tertiary butyl alcohol was completely removed additional dry carbon tetrachloride was added and the mixture was again concentrated to 500 ml.

Oxidation of cholesteryl acetate. A solution of 51 g. of cholesteryl acetate and 250 ml. of dry carbon tetrachloride was heated to 80° and with good stirring 500 ml. of tertiary butyl chromate solution (prepared by the method described) along with 125 ml. of glacial acetic acid and 50 ml. of acetic anhydride was added over a period of about 45 min. After completion of the addition, the mixture was stirred at 80° for 10 hr. After cooling in an ice bath, a solution of 75 g. of oxalic acid dihydrate in 750 ml. of water was added over a period of 1 hr. During the addition, the dark brown, emulsified solution was kept below 10°. Fifteen min. after completion of the addition, 75 g. of crystalline oxalic acid dihydrate was added in 4 portions. The mixture was stirred for 2 hr. at room temperature. To eliminate troublesome emulsion formation, Super Cel was added to the reaction mixture and it was filtered through a thick mat of Super Cel. The layers were separated and the aqueous layer was extracted 3 times with carbon tetrachloride. The combined organic fractions were washed with water (twice), 250 ml. of 10% potassium bicarbonate solution, and finally twice with water. The carbon tetrachloride solution was dried over anhydrous magnesium sulfate with the addition of a small amount of acetic anhydride and pyridine. The solution was filtered and evaporated under reduced pressure. The residue after drying in a vacuum oven, gave crude 7-keto cholesteryl acetate (39.8 g.). m.p. 143–147°. Recrystallization from ethanol afforded 34 g. (64.3%) of pure 7-keto cholesteryl acetate, m.p. 159–161°; ultraviolet; λ_{max}^{MeOH} 235 mμ (ε, 12,000).

(*B*) *Sodium chromate method.*[9] To a solution of 40 g. of cholesteryl acetate in 280 ml. of glacial acetic acid, 160 ml. of acetic anhydride and 24 g. of sodium acetate, cooled to 35° (thick slurry) there was added portionwise 35 g. of sodium chromate with intermittent cooling to maintain the mixture in the range 30–40°. The reaction mixture was stirred for 46 hr. at 50–60°. During this period (at approximately 8-hr. intervals) a 5-ml. aliquot was drawn off and quenched in ice water. The product that separated was washed thoroughly with water, dried to constant weight, and submitted for infrared analysis. As the reaction time progressed the carbonyl band at 5.95 μ (1681 cm.$^{-1}$) became more intense and by comparison with the infrared spectrum of an authentic sample it was possible to determine qualitatively the completeness of the reaction. After cooling, the reaction mixture was poured into 3.5 l. of cold water. This mixture was stirred at 10° for 1 hr., filtered, and the product collected was washed with water and dried to constant weight (25.5 g.) m.p. (crude) 145–152°. Recrystallization from ethanol gave 21.0 g. (50.6%) of 7-keto cholesteryl acetate, m.p. 157–159°.

Cholesta-3,5-dien-7-one (VIII).[10,11] Fifty-three g. of 7-keto cholesteryl acetate (VII) in 1080 ml. of absolute ethanol containing 53 ml. of dilute hydrochloric acid was maintained at the reflux temperature for 1 hr. After cooling in ice the crude dieneone that separated was filtered and washed well with cold water (36 g.), m.p. (crude) 106–110°. The mother liquor was concentrated *in vacuo* to a small volume and after cooling in ice a second crop was obtained (6.5 g.), m.p. (crude) 102–111°. The two crops were combined and recrystallized from 95% ethanol (35.4 g.) (77.6%) m.p. 109–119°.

ψ-Cholesterol (IX). Forty-five g. of cholesta-3,5-dien-7-one (VIII) and 1 l. of dry 1-propanol were heated to boiling and 72 g. of metallic sodium was added over a period of 4.5 hr. At first the solution turned a dark green but later it became colorless. After the addition was completed the mixture was held at the reflux temperature one additional hour, cooled, and poured into 3 l. of cold water. This mixture was extracted 3 times with ether. The combined ether extracts were washed twice with water and dried overnight with anhydrous magnesium sulfate. The solvent was removed *in vacuo* and the resulting product was collected and dried (34.2 g.), m.p. (crude) 110–116°. Recrystallization from acetone-methanol (1:1) gave 29 g. (63.7%) m.p. 116.5–117.5°. Analytical sample was prepared by repeated recrystallization from acetone-methanol (1:1). m.p. 118.8–120.4°.

Anal. Calcd. for $C_{27}H_{46}O$: C, 83.87; H, 11.99. Found: C, 83.73; H, 12.16.

Cholest-4-en-7-one (X). A solution of 5 g. of ψ-cholesterol (IX) and 550 ml. of purified acetone was cooled to 10–15° and with stirring under an atmosphere of nitrogen, 5.6 ml. of standard chromate reagent[26] was rapidly added. After 5 min. the reaction mixture was poured into a saturated aqueous sulfur dioxide solution, followed by the addition of

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(25) All melting points were taken by capillary and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 21 double-beam spectrophotometer in carbon tetrachloride. Ultraviolet spectra in methanol were obtained through the courtesy of Merck & Co., Rahway, N. J. Optical rotations were determined in a 1-dm. semimicro tube. Analyses were performed by J. F. Alicino, Metuchen, N. J.

(26) Standard chromate solution—26.72 g. of chromium trioxide in 23 ml. of concentrated sulfuric acid, diluted with water to a volume of 100 ml.

saturated aqueous potassium carbonate and ether. The ether layer was separated and the aqueous phase was extracted 3 times with ether. The combined ethereal extracts were washed twice with water, dried over anhydrous sodium sulfate, and taken to dryness *in vacuo*. The residue was recrystallized from acetone-water to give 3.84 g. (77.3%) of crude product, m.p. 93–98°; infrared: 5.84 μ (1712 cm.$^{-1}$) (strong), 5.96 μ (1679 cm.$^{-1}$) (very weak); ultraviolet; λ_{max}^{MeOH} 245 mμ (ϵ, 679).

The material prepared above was used in the subsequent steps without further purification but in order to obtain an analytical sample the oxidation product was chromatographed on acid-washed alumina (Merck). Elution with petroleum ether–benzene (4:1) gave material which was recrystallized 3 times from acetone, m.p. 100.2–101.8°; $[\alpha]_D^{23}$ −8.5° (c, 0.927 in chloroform); infrared: 5.84 μ (1712 cm.$^{-1}$) (strong), no absorption at 5.96 μ (1679 cm.$^{-1}$); ultraviolet: no appreciable absorption in the 200–300 mμ region.

Anal. Calcd. for $C_{27}H_{44}O$: C, 84.31; H, 11.53. Found: C, 84.46; H, 11.46.

Epi-ψ-cholesterol (XI). A solution of 1 g. of cholest-4-en-7-one (X) in 56 ml. of methanol and 14 ml. of ether was added dropwise (30 min.) to a solution of 926 mg. of sodium borohydride in 8 ml. of water and 32 ml. of methanol. This reaction mixture was stirred at room temperature for 22 hr. and then heated at the reflux temperature for 2 additional hours. After cooling, ether was added and the solution acidified with 5% hydrochloric acid until acid to Congo red. The ethereal layer was separated and the aqueous phase extracted 3 times with ether. The combined ethereal extract was washed once with 5% hydrochloric acid, twice with water, and dried overnight with anhydrous sodium sulfate. The solvent was removed *in vacuo* and a clear colorless oil was obtained which crystallized with scratching. The crude product was filtered, washed with cold water, and dried overnight in a vacuum oven to give 954 mg. m.p. (crude) 68–90°. This was chromatographed on 28 g. of neutral alumina.

Epi-ψ-cholesteryl acetate. One hundred and fifty mg. of epi-ψ-cholesterol (XI) was dissolved in 1.0 ml. of acetic anhydride and heated on the steam bath for 1.5 hr. The product that separated upon cooling was collected and recrystallized once from acetone and twice from ethanol, 123 mg., m.p. 101.4–102.2°; $[\alpha]_D^{23}$ +4.31 (c, 1.23 in chloroform); infrared: 5.75 μ (1739 cm.$^{-1}$) 8.03 μ (1245 cm.$^{-1}$).

Anal. Calcd. for $C_{29}H_{48}O_2$: C, 81.27; H, 11.28. Found: C, 81.24; H, 11.34.

Epi-ψ-cholesteryl-p-toluenesulfonate (XII). To 2.5 g. of epi-ψ-cholesterol (XI) in 75 ml. of dry pyridine (distilled over barium oxide) was added portionwise 6.75 g. of *p*-toluenesulfonyl chloride[27] over a period of 0.5 hr. at 0°. After 2 hr. at 0° the mixture was kept 3 days at room temperature. Ice was added and the mixture set aside for 1.5 hr. the solution was extracted 3 times with ether and the combined ethereal extract was washed once with cold 2*N* hydrochloric acid, once with saturated sodium bicarbonate, and finally with water. The solution was dried over anhydrous magnesium sulfate and concentrated to dryness *in vacuo*. The white residue was recrystallized twice from acetone, 1.73 g. (49.5%), m.p. 92.6–93.0° (at 105–108° turned blood red) $[\alpha]_D^{23}$ −7.53° (c, 1.12 in chloroform); infrared: 7.30 μ (1370 cm.$^{-1}$) 8.45 μ (1183 cm.$^{-1}$).

Anal. Calcd. for $C_{34}H_{52}O_3S$: C, 75.51; H, 9.69; S, 5.90. Found: C, 75.32; H, 9.74; S, 5.86.

Acetoylysis of epi-ψ-cholesteryl tosylate with potassium acetate–acetic acid. A solution of 500 mg. of epi-ψ-cholesteryl tosylate (XII) and 800 mg. of anhydrous potassium acetate in 24 ml. of glacial acetic acid was heated at 95° for 4 hr. After 30 min. the solution turned yellow and at the end of the 4 hr. period it was a dark orange. After the acetic acid was removed by evaporating to dryness *in vacuo*, the product was taken up in an ether-water mixture. The aqueous phase was separated and washed 3 times with ether. The combined ethereal extracts were washed twice with 10% sodium bicarbonate solution and 3 times with water, dried over anhydrous sodium sulfate, and taken to dryness *in vacuo*. Three hundred and seventy three mg. of a yellow oil was obtained which was chromatographed on 20 g. of neutral alumina. Elution with pentane (Fractions 2–10) gave 296 mg. (73.4%) of cholesta-4,6 diene (IV) which was recrystallized from ether, m.p. 86.5–89.0° $[\alpha]_D^{23}$ +9.2° (c, 0.83 in

Fraction	Solvent Mixture	Weight, Mg.	Character	Melting Point, °C.
11	Benzene:Et_2O 3:2	Trace		
12		34	White crystals	84–86.5
13	Benzene:Et_2O 1:1	91		84–86
14	Benzene:Et_2O 1:1	87	White crystals	
15		84		83.5–85.5
16		62		
17		78		84–86
18		131		83.5–85.5
19	Benzene:Et_2O 2:3	108		
20		72		83–85.5
21		55		79–83
22		31		75–80
23		21		75–80
24		47		91–105
25		22		110–118
26		Trace	Yellow-green crystals	

Fractions 12–21 were combined and recrystallized 3 times from acetone, 602 mg. m.p. 85–87°, infrared: 2.78 μ (3600 cm.$^{-1}$), 9.00 μ (1111 cm.$^{-1}$) 9.70 μ (1031 cm.$^{-1}$). An analytical sample was prepared by recrystallizing 3 times from acetone, m.p. 85.0–86.2° $[\alpha]_D^{23}$ +44.46° (c, 0.931 in chloroform).

Anal. Calcd. for $C_{27}H_{46}O$: C, 83.87; H, 11.99. Found: C, 83.93; H, 12.02.

Fractions 24–25 were recrystallized twice from acetone-methanol (1:1) to give a product with a melting point of 116–118°. This was shown to be identical to ψ-cholesterol by mixed melting point and infrared comparison.

(27) The *p*-toluenesulfonyl chloride was purified in the following manner: An ether solution of *p*-toluenesulfonyl chloride was washed with 2*N* Na_2CO_3 and with water, dried over anhydrous magnesium sulfate, and evaporated to dryness. The product was recrystallized twice from benzene and after drying to constant weight was sealed in small ampoules under an atmosphere of nitrogen.

chloroform); ultraviolet; λ_{max}^{MeOH} 230 mμ; ε, 17,820; log ε 4.25: λ_{max}^{MeOH} 237 mμ; ε, 19,290; log ε, 4.29: λ_{max}^{MeOH} 245.5 mμ; ε, 12,250; log ε, 4.09.

Anal. Calcd. for $C_{27}H_{44}$: C, 87.98; H, 12.02. Found: C, 87.74; H, 12.14.

Elution with benzene-ether (4:1) (Fractions 20–23) gave a small amount of a compound which had all the properties of cholesteryl acetate indicating that the double bond in the 4–5 position is playing a role in the solvolysis.

Hydrolysis of epi-ψ-cholesteryl tosylate. To a solution of 500 mg. of epi-ψ-cholesteryl tosylate (XII) in 35 ml. of purified acetone and 9 ml. of water was added 1.4 g. of anhydrous potassium acetate. This mixture was held at the reflux temperature for 9 hr., cooled, and poured into water. This aqueous solution was extracted 3 times with ether and the combined ethereal extracts were washed 3 times with water and dried over magnesium sulfate. Concentration *in vacuo* gave a clear oil, (340 mg.) which was chromatographed on 12 g. of neutral alumina. Elution with pentane (Fractions 3–13) gave 248 mg. (61.5%) of crystalline product which was recrystallized from acetone, m.p. 87.5–90.2. Examination of the infrared and ultraviolet spectra showed that this product was identical to cholesta-4,6-diene (IV). Elution with benzene-ether (4:1) (Fractions 25–27) gave a white crystalline product, 23 mg. (5.4%), m.p. 85.2–87.1° $[\alpha]_D^{23}$ +58° (c, 0.981 in chloroform).

Anal. Calcd. for $C_{27}H_{46}O$: C, 83.87; H, 11.99. Found: C, 83.96; H, 11.94. From an examination of the physical data and the infrared spectrum, this compound was assigned the structure of cholest-4-en-6β-ol (XIII). Further elution with benzene-ether (4:1) (Fractions 28–32) gave 40 mg. (9.5%) of a white crystalline product, m.p. 129.5–132°; $[\alpha]_D^{23}$ −55.2° (c, 1.19 in chloroform).

Anal. Calcd. for $C_{27}H_{46}O$: C, 83.87; H, 11.99. Found: C 83.59; H, 11.72. The physical data and the infrared spectrum of this compound suggest that it is cholest-5-en-4β-ol (XIV).

Acetolysis of epi-ψ-cholesteryl tosylate with potassium acetate–acetic anhydride mixture. To a solution of 1.43 g. of anhydrous potassium acetate and 24 ml. of acetic anhydride at 50° was added 500 mg. of epi-ψ-cholesteryl tosylate (XII) in several portions. This mixture was stirred at 75° for 38 hr. (yellow coloration). After concentration to dryness the residue was taken up in ether-water mixture and the layers separated. The aqueous phase was washed 3 times with ether and the combined ethereal extract was washed once with a 10% sodium bicarbonate solution and twice with water. The ethereal solution was dried over anhydrous magnesium sulfate and taken to dryness *in vacuo* to give 283 mg. (70.2%) of a dark yellow solid which was chromatographed on 14 g. of neutral alumina. Elution with pentane (Fractions 2–11) gave 250 mg. (62%) of a white crystalline solid which was recrystallized from acetone, m.p. 85.5–91.0°. Examination of the infrared and ultraviolet spectra showed that this material was identical to cholesta-4,6-diene(IV).

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Reaction of the Enol Form of 1,2-Cyclohexanedione with the Phenyl Grignard Reagent[1]

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Spectroscopic evidence indicates that 4-, 5-, and 6-membered 1,2-cycloalkanediones exist exclusively in the enol form. 2-Hydroxy-2-cyclohexen-1-one reacts with the phenyl Grignard reagent to form the conjugate addition product, 2-hydroxy-3-phenylcyclohexanone. Treatment of this compound with the phenyl Grignard reagent results in the formation of 1,3-diphenyl-1,2-cyclohexanediol. The structures of these adducts are established by oxidative degradation.

The nature of the keto-enol equilibrium in 1,2-diketones has been the subject of considerable discussion, but with the advent of spectroscopic methods, investigations have established with certainty which of the tautomers predominates. Selected absorption maxima for various ketones are presented in Table I. The conjugated ketone chromophore (as exemplified by isophorone) absorbs near 235 mμ with a relatively high intensity. This same feature is found (with a bathochromic shift) in the ultraviolet spectra of all enolic 1,2-diketones. Characteristic infrared absorptions also identify these conjugated systems; the C=C stretching vibration occurs near 1640 cm.$^{-1}$ and the conjugated C=O absorption near 1670 cm.$^{-1}$

On the other hand, the 1,2-diketones which cannot enolize, such as camphorquinone[17] and 3,3,6,6-tetramethyl-1,2-cyclohexanedione, exhibit completely different spectra. The ultraviolet and visible absorption of the diketone chromophore is characterized by a relatively weak, broad band in the 380–450 mμ region. The infrared carbonyl absorption frequency is near the normal position. In a series of substituted 1,2-cycloalkanediones in which the ring contained from nine to fourteen carbon atoms,[18] the carbonyl absorptions were in the range 1704–1708 cm.$^{-1}$. Thus, from an examination of the

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