Wolff–Kishner Reduction of the d_3-4,4-Dimethylestr-5-en-17β-ol-3-one Acetates.—The crude crystalline alkylated material (24 mg), mp 125–130°, obtained by d_3-methylation of 4-methyl-19-nortestosterone acetate (9) was reduced with a solution of sodium (200 mg) and hydrazine (0.6 ml) in diethylene glycol (3 ml). Analogous treatment as described above gave an oily material (27 mg) which was chromatographed on alumina (8 g.) Elution with pentane–ether (13:1) gave 8 mg of material, mp 144–146°, which consisted mainly of 4β-methyl-d_3-4α-methylestr-5-en-17β-ol acetate (17) (see discussion).

Mass Spectrometry in Structural and Stereochemical Problems. XCI.[1] The Electron Impact Induced Elimination of Water from 3-Hydroxy Steroids

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One of the ubiquitous fragmentation modes of 3-hydroxy steroids is the loss of 33 mass units (methyl radical plus water). By deuterium labeling in the cholestane series it could be shown that in the case of the axial 3α-alcohol the M − 15 ion loses water exclusively by 1,3 elimination of the hydroxyl function and the 1α- and the 5α-hydrogen atoms, respectively. The 3β-alcohol shows more random loss of water after elimination of the C-19 methyl group. An explanation for this apparently inconsistent behavior is given.

Studies of cyclic alcohols (cyclopentanol[2] and cyclohexanol[3,4]) have shown that electron impact induced loss of water occurs as a 1,3 or 1,4 elimination. However, it could not be determined with these model compounds whether this reaction occurs in a stereospecific manner. In the steroid series studies of this type seemed feasible and our results are reported herewith.

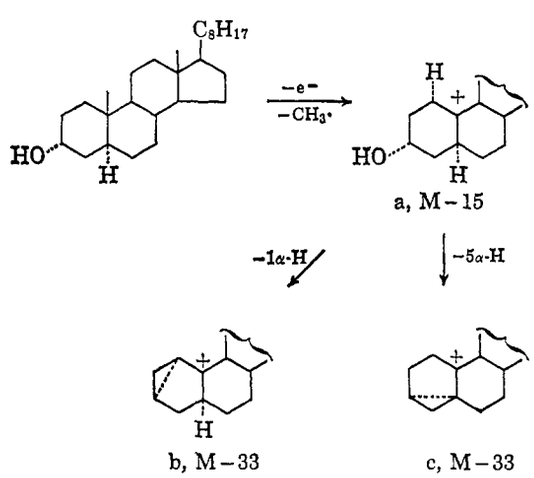
The spectrum of 5α-androstan-3β-ol shows a prominent M − 18 peak and would, therefore, have been suitable for our studies. We wanted, however, to rule out any possible falsification of the results by thermal loss of water prior to electron impact and chose, therefore, a different substance. The M − 18 fragment in the case of cholestan-3α- and -3β-ol is negligible when direct insertion of the sample in the ion source is used.[5,6] However, loss of water can be observed (see Figure 1) starting from the M − 15 fragment (supported by appropriate metastable ion at *m/e* 338.0, calcd 337.8), and we chose this process for our further studies.

The data obtained with various deuterium-labeled analogs of cholestan-3α-ol are given in Table I (the estimated error is ±2%). These results show that no 1,2 elimination occurs in this fragmentation process. Most of the deuterium lost stems from the 5α-position, while comparison of the 1,1,3β-d_3 and the 1α-d_1 analogs shows that some deuterium comes from the 1α-position. Assuming that the total (about 80%) accounts for all the loss of water from the M − 15 species, an isotope effect of 0.8 has to be invoked which lies well within the observed range.[7,8] The driving force of this sequence is apparently the stabilization of the C-19 carbonium ion by conjugation with a cyclopropane ring. Preferential loss of the 5α-hydrogen (from a tertiary position) compared with the secondary 1α locus has its parallel in other fragmentations.[9]

TABLE I

ORIGIN (%) OF HYDROGEN IN M − 34 FRAGMENT OF LABELED CHOLESTAN-3α-OLS

Compound	M − 34 (CH_3 + HDO)
Cholestan-3α-ol	0
Cholestan-3α-ol-2,2,4,4-d_4 (V)	0
Cholestan-3α-ol-1,1,3β-d_3 (XIX)	7 ± 2
Cholestan-3α-ol-1α-d_1 (IX)	4.5 ± 2
Cholestan-3α-ol-5α-d_1 (XIII)	73 ± 2



The analogous data for the isomeric cholestan-3β-ol are compiled in Table II and show that this compound follows different fragmentation paths. No loss of deuterium is observed from the 1α-, 2-, 3α-, or 4-positions, while elimination from the 1β- and 5α-(!) position totals only about 40%. On the assumption that the same isotope effect operates as in the 3α-hydroxy isomer, only about one-half of the loss of water from the M − 15 ion is accounted for and the remaining hydrogen must be abstracted from carbon atoms other than in ring A.

(1) Paper XC: A. H. Jackson, G. W. Kenner, H. Budzikiewicz, C. Djerassi, and J. M. Wilson, *Tetrahedron*, in press.

(2) P. Natalis, *Bull. Soc. Chim. Belges*, **69**, 224 (1960).

(3) C. G. McDonald, J. S. Shannon, and G. Sugowdz, *Tetrahedron Letters*, 807 (1963).

(4) H. Budzikiewicz, Z. Pelah, and C. Djerassi, *Monatsh.*, **95**, 158 (1964).

(5) J. F. Lynch, J. M. Wilson, H. Budzikiewicz, and C. Djerassi, *Experientia*, **19**, 211 (1963).

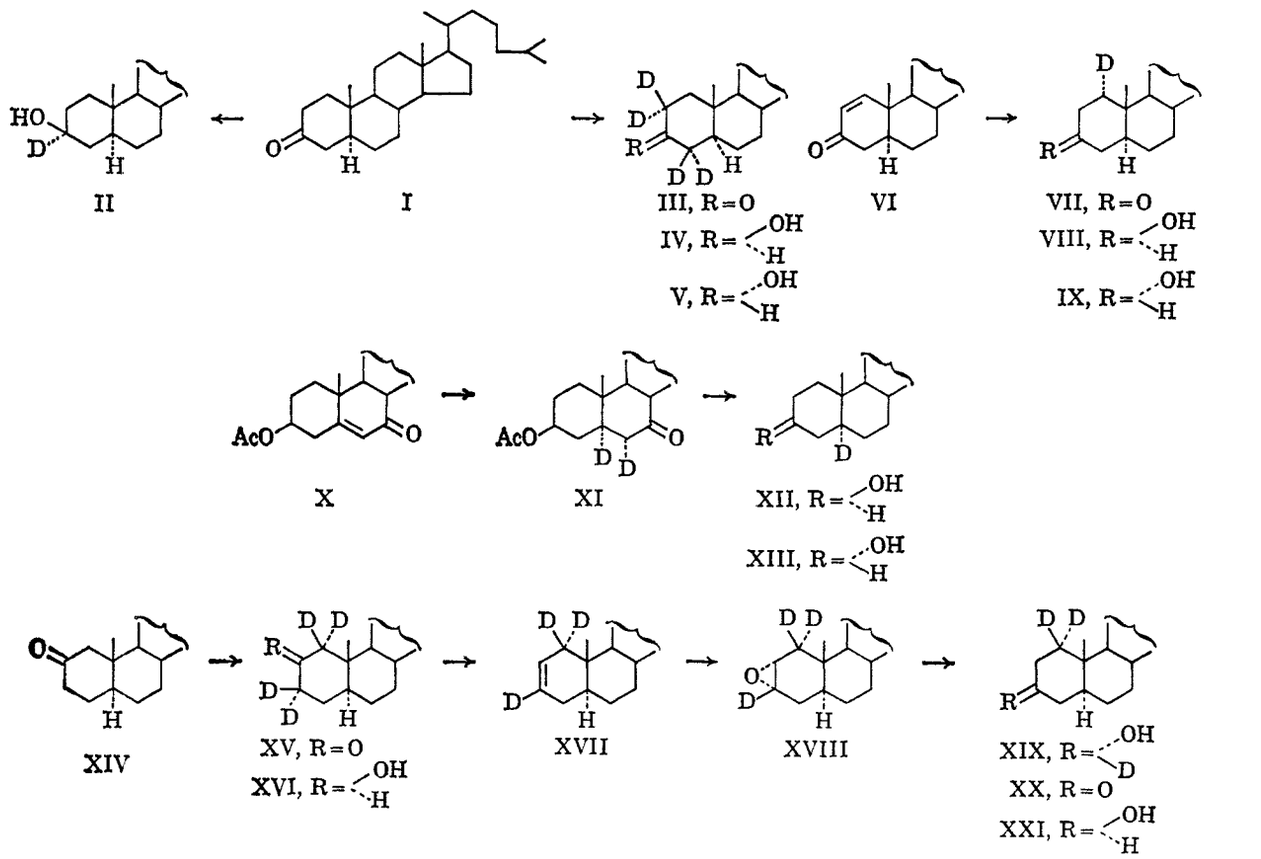
(6) Using the conventional heated all-glass inlet system, a substantial M − 18 peak is observed in the mass spectrum which must be due to thermal loss of water, since the 2,2,4,4-d_4 analogs showed that here entirely 1,2 elimination occurred.

(7) D. H. Williams, H. Budzikiewicz, and C. Djerassi, *J. Am. Chem. Soc.*, **86**, 284 (1964).

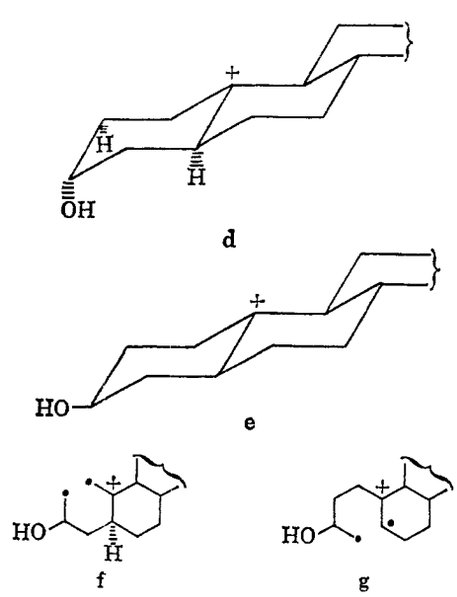
(8) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press Inc., New York, N. Y., 1957, Chapter 5.

(9) C. Beard, J. M. Wilson, H. Budzikiewicz, and C. Djerassi, *J. Am. Chem. Soc.*, **86**, 269 (1964).

SCHEME I



The explanation for this apparently inconsistent behavior of the 3α and 3β isomers may be found in the observation that in the former the oxygen atom and the 1α- and 5α-hydrogens are close enough (d) to allow interaction and thus elimination. In the chair form (e) of the 3β isomer, no such interaction is possible and even in the boat form only the 1β-hydrogen can approach the hydroxyl oxygen sufficiently. Stabilization of the positive charge at C-10 in the M − 15 ion of cholestan-3β-ol seems, therefore, to occur largely by different processes, such as by the rupture of the 1,2 bond or preferentially the more highly substituted 4,5 linkage, yielding ionized double bonds, f and g.



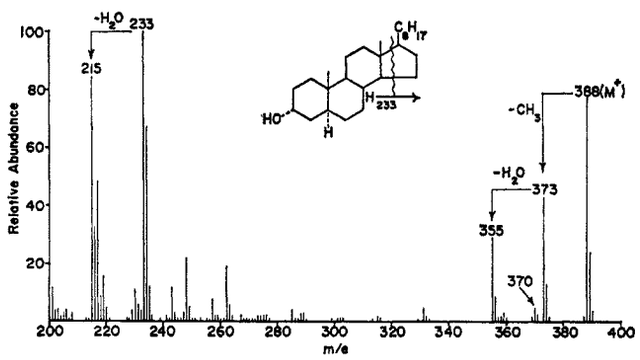


Figure 1.—Partial mass spectrum (high mass range) of 5α-cholestan-3α-ol.

TABLE II

ORIGIN (%) OF HYDROGEN IN M − 34 FRAGMENT OF LABELED CHOLESTAN-3β-OLS

Compound	M − 34 (CH_3 + HDO)
Cholestan-3β-ol	0
Cholestan-3β-ol-2,2,4,4-d_4 (IV)	0
Cholestan-3β-ol-3α-d_1 (II)	0
Cholestan-3β-ol-5α-d_1 (XII)	11
Cholestan-3β-ol-1,1-d_2 (XXI)	28
Cholestan-3β-ol-1α-d_1 (VIII)	0

Owing to the open ring A in f and g, loss of water is now possible from carbon atoms other than ring A and this may explain the results listed in Table II. This observation confirms a conclusion reached before that apparently minor structural differences may cause strikingly different fragmentation paths (*cf.* ref 10)

(10) H. Budzikiewicz, J. I. Brauman, and C. Djerassi, *Tetrahedron*, **21**, 1855 (1965).

if stabilization of the positive charge in the molecular ion is favored in an alternate manner.

The labeled compounds discussed in this paper were prepared as indicated in Scheme I.

Experimental Section[11]

5α-Cholestan-3β-ol-3α-d_1 (II).—The procedure described by Wheeler and Mateos[12] for the stereospecific reduction of 3-keto steroids was used, except that lithium aluminum hydride was substituted by lithium aluminum deuteride. After recrystallization from methanol, the colorless crystals exhibited mp 142–143°; mass spectrum, *m/e* 388 (d_0), 2%; *m/e* 389 (d_1), 98%.

5α-Cholestan-3β-ol-2,2,4,4-d_4 (IV) and 5α-Cholestan-3α-ol-2,2,4,4-d_4 (V).—To a refluxing mixture of 370 mg of 5α-cholestan-3-one and 150 mg of sodium methoxide in 6 ml of O-deuteriomethanol and 3 ml of deuterium oxide was added dioxane until a homogeneous solution resulted, and the latter was heated under reflux overnight in an atmosphere of nitrogen. The cooled solution was evaporated, 1.5 ml of deuterium oxide and 10 ml of anhydrous ether were added, and the aqueous phase was removed with a pipet. The ethereal solution was dried over anhydrous magnesium sulfate, filtered, and added directly to a stirring suspension of 200 mg of lithium aluminum hydride in diethyl ether. After heating under reflux in a nitrogen atmosphere for 2 hr, excess hydride was decomposed by the dropwise addition of water, dilute hydrochloric acid was added, and the mixture was poured into water and extracted with ether. The ether extract was washed with water, 5% sodium bicarbonate, and water and dried over anhydrous magnesium sulfate. Evaporation of the solvent afforded a mixture of tetradeuteriocholestanol and tetradeuterioepicholestanol which was chromatographed over 60 g of neutral alumina, activity II. Elution with 1:1 ether–benzene provided 21 mg of V. Recrystallization from methanol afforded crystals melting at 185.5–187°: mass spectrum, *m/e* 391 (d_3), 22%; *m/e* 392 (d_4), 78%. Increasing the polarity of the eluent to 3:2 ether–benzene furnished 160 mg of 5α-cholestan-3β-ol-2,2,4,4-d_4 (IV) melting at 142.5–143° after recrystallization from methanol: mass spectrum, *m/e* 391 (d_3), 21%; *m/e* 392 (d_4), 79%.

5α-Cholestan-3-one-1α-d_1 (VII).—A suspension of 195 mg of Δ^1-5α-cholesten-3-one and 50 mg of 10% palladium on charcoal was stirred in the presence of deuterium gas for 48 hr.[13] The catalyst was filtered and the solvent was evaporated under diminished pressure to furnish 5α-cholestan-3-one-1α,2α-d_2:[14] identical with 5α-cholestan-3-one by thin layer chromatographic analysis; infrared spectrum, 4.72 (C–D) and 5.87 μ (C=O).

The crude dideuterio ketone was heated under reflux for 5 hr in 30 ml of 10% methanolic potassium hydroxide; the cooled reaction mixture was evaporated almost to dryness and then taken up in ether. The ethereal solution was washed with water, dilute hydrochloric acid, water, 5% sodium bicarbonate, and water. After drying over anhydrous magnesium sulfate, the solvent was removed under reduced pressure to afford 185 mg of product (VII). Recrystallization from methanol afforded 5α-cholestan-3-one-1α-d_1, melting at 128.5–129.5°.

5α-Cholestan-3β-ol-1α-d_1 (VIII) was prepared as described in the preparation of II by lithium tri-*t*-butoxyaluminohydride[15] reduction of 62 mg of VII to furnish 60 mg of 5α-cholestan-3β-ol-1α-d_1 (VIII): mp 142.5–143.5° after recrystallization from methanol; mass spectrum, *m/e* 388 (d_0), 20%; *m/e* 389 (d_1), 78%; *m/e* 390 (d_2) 2%.

5α-Cholestan-3α-ol-1α-d_1 (IX).—Epimerization of the 3β-hydroxy group was accomplished by the method described by Plattner and Fürst.[16] 5α-Cholestan-3β-ol-1α-d_1 (28 mg) was transformed into the tosylate and the crude product was dissolved in 3 ml of glacial acetic acid and 35 mg of anhydrous sodium acetate. After heating under reflux for 1 hr, the solvent was evaporated and the remaining oil was taken up in ether–water. After washing the organic phase with water, 5% sodium bicarbonate, and water and drying over anhydrous magnesium sulfate, the solvent was removed under diminished pressure to furnish 31 mg of crude 5α-cholestan-3α-ol-3α-d_1 acetate. This material was treated directly with excess lithium aluminum hydride in ether and heated under reflux for 3 hr. The usual work-up afforded 26 mg of a mixture of 5α-cholestan-3α-ol-1α-d_1, 5α-cholestan-3β-ol-1α-d_1, and less polar material (most probably a mixture of olefins), determined by thin layer comparison with the corresponding nondeuterated species. The desired 5α-cholestan-3α-ol-1α-d_1 (12 mg, 41.5% from VIII) was obtained by preparative thin layer chromatography using a 3:1 benzene–ether solvent system: mass spectrum, *m/e* 388 (d_0), 21%; *m/e* 389 (d_1), 77%; *m/e* 390 (d_2), 2%.

5α-Cholestan-3β-ol-5α-d_1 (XII).—A suspension of 350 mg of X[17] and 165 mg of 10% palladium on carbon in cyclohexane was stirred in the presence of deuterium gas at 20° for 1.25 hr. Filtration of the catalyst and evaporation of the solvent provided a colorless material which showed, in addition to the expected product, XI, a more polar substance on a thin layer chromatoplate, which was shown by infrared spectroscopy to be due to reduction of the 7-keto group to an alcohol. Treatment of the crude product with Jones[18] reagent gave a homogeneous, crystalline solid (XI) whose infrared spectrum (4.63–4.76, 5.78, 5.83, and 8.03 μ) was consistent with the assigned structure.

The dideuterioketo acetate XI was back-exchanged without purification by treating under reflux for 3 hr with 65 ml of 1% methanolic potassium hydroxide. Evaporation of the cooled solution afforded a residue which was taken up in ether–water; the ethereal solution was washed with 5% hydrochloric acid, water, 5% sodium bicarbonate, and water, and dried over anhydrous magnesium sulfate. Removal of solvent furnished 300 mg of 5α-cholestan-3β-ol-7-one-5α-d_1.

The back-exchanged product (298 mg) and 2.2 ml of 95% hydrazine in 10 ml of ethanol and 15 ml of diethylene glycol was heated under reflux in a nitrogen atmosphere for 1 hr.[19] Solid potassium hydroxide (1.7 g) was added and heating under reflux was continued for an additional 0.5 hr. The reflux condenser was removed and the reaction mixture was heated until an internal temperature of 188° was attained, whereupon the solution was heated under reflux at 195–202° under nitrogen for 4 hr. The cooled solution was poured into water and extracted with ether, and the ethereal solution was washed with water, dilute hydrochloric acid, water, 5% sodium bicarbonate, and water. After drying over anhydrous magnesium sulfate, solvent was removed under reduced pressure to provide 285 mg of product, XII. Recrystallization from methanol gave pure 5α-cholestan-3β-ol-5α-d_1 (XII): mp 143–144°; mass spectrum, *m/e* 388 (d_0), 9%; *m/e* 389 (d_1), 89%; *m/e* 390 (d_2), 2%.

5α-Cholestan-3α-ol-5α-d_1 (XIII).—This material was obtained by the usual[16] acetolysis of the tosylate: mp 187.5–188.5°; mass spectrum, *m/e* 388 (d_0), 8%; *m/e* 389 (d_1), 89%; *m/e* 390 (d_2), 3%.

5α-Cholestan-2-one-1,1,3,3-d_4 (XV).—5α-Cholestan-3-one was converted to 5α-cholestan-2-one as described for the similar transformation in the androstane series.[20] A solution of 480 mg of XIV in 15 ml of O-deuteriomethanol and 7 ml of dioxane was heated under reflux in a nitrogen atmosphere, 250 mg of sodium methoxide in 3 ml of deuterium oxide was added, followed by dropwise addition of dioxane until a homogeneous solution resulted, and the latter was heated under reflux in an atmosphere of nitrogen for 1 week. Work-up as described above for the preparation of 5α-cholestan-3-one-2,2,4,4-d_4 afforded only partially exchange product (*ca.* 60% d_4). Repeating the equilibration experiment for an additional week afforded 5α-cholestan-2-one-1,1,3,3-d_4 (XV): mp 128.5–129.5° after recrystallization

(11) The mass spectra were determined with a Consolidated Electrodynamics Corp. mass spectrometer, No. 21-103C, equipped with a direct inlet system.[5] The ionizing current was kept at 50 μa, while the ionizing energy was maintained at 70 ev and the source temperature at 250°. Melting points were determined on a Kofler hot stage and are uncorrected. Analytical thin layer chromatoplates with a thickness of 0.25 mm of silica gel G (E. Merck A.G., Darmstadt) were used and the spots were detected by spraying with a 2% ceric sulfate solution in 2 *N* sulfuric acid. Preparative thin layer chromatoplates had a thickness of 0.50 mm of silica gel HF_{254} (E. Merck A.G., Darmstadt) and compounds were detected by viewing under ultraviolet light.

(12) O. H. Wheeler and J. L. Mateos, *Can. J. Chem.*, **36**, 1431 (1948).

(13) F. Schmitz and W. S. Johnson, *Tetrahedron Letters*, 647 (1962); H. J. Ringold, M. Gut, M. Hayano, and A. Turner, *ibid.*, 835 (1962).

(14) Catalytic deuteriation of Δ^1-5α-cholesten-3-one has been shown to introduce deuterium from the α face. See ref 13.

(15) H. C. Brown and R. F. McFarlin, *J. Am. Chem. Soc.*, **78**, 252 (1956).

(16) P. A. Plattner and A. Fürst, *Helv. Chim. Acta*, **26**, 2266 (1943).

(17) K. Heusler and A. Wettstein, *ibid.*, **35**, 284 (1952).

(18) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

(19) Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).

(20) J. E. Gurst and C. Djerassi, *ibid.*, **86**, 5542 (1964), and references therein.

from O-deuteriomethanol; mass spectrum, *m/e* 389 (d_3), 19%; *m/e* 390 (d_4), 81%.

5α-Cholestan-2β-ol-1,1,3,3-d_4 (XVI) was prepared by lithium tri-*t*-butoxyaluminum hydride[15] reduction of XV as described for the analogous formation of II to provide 5α-cholestan-2β-ol-1,1,3,3-d_4 and a trace of the 2α isomer. Recrystallization of a portion from methanol gave the pure 2β-alcohol, mp 152–154° (for unlabeled alcohol, see ref 21).

Δ²-5α-Cholestene-1,1,3-d_3 (XVII).—The above mixture (465 mg) of 5α-cholestan-2β-ol-1,1,3,3-d_4 and its C-2 epimer was treated with *p*-toluenesulfonyl chloride in pyridine for 25 hr at room temperature and the semisolid which was isolated in the usual manner was dehydrotosylated by heating in 10 ml of dimethyl sulfoxide at 100–103° for 5 hr.[22] The cooled solution was poured into water and extracted with ether, and the ethereal extract was washed with water, 5% sodium bicarbonate (three times), and water (two times), and dried over anhydrous magnesium sulfate. Ether was removed under reduced pressure and a small amount of dimethyl sulfoxide that remained was removed by evaporation at vacuum-pump pressure (0.1 mm). The remaining oil was chromatographed over 60 g of neutral alumina, activity II. Petroleum ether (bp 60–68°) elution furnished 186 mg of Δ²-5α-cholestene-1,1,3-d_3 (XVII), mp 72.5–73° after recrystallization from acetone. Elution with 20% ether in benzene afforded 85 mg of unreacted starting material XVI (mp 155–156° from methanol), and further increasing the eluent polarity to 35% ether in benzene provided 30 mg of 5α-cholestan-2α-ol-1,1,3,3-d_4 (mp 180–181° from methanol).

5α-Cholestan-3α-ol-1,1,3β-d_3 (XIX).—To a solution of 130 mg of XVII in 4 ml of anhydrous ether was added a solution of 85 mg of *m*-chloroperbenzoic acid in 3 ml of anhydrous ether, and the resulting homogeneous solution was kept at room temperature in the dark for 3 days. The ethereal solution was washed well with 5% sodium bicarbonate and water and dried over anhydrous magnesium sulfate. Evaporation of the solvent afforded 132 mg of crystalline material (2α,3α-oxido-5α-cholestane-1,1,3-d_3[21]) which was not purified further but was converted directly to 5α-cholestan-3α-ol-1,1,3β-d_3 (XIX) by heating under reflux for 3 hr with excess lithium aluminum hydride in ether.[21] The crude reduction product was purified by chromatography over 20 g of neutral alumina, activity II, using benzene as eluent, giving 63 mg of crystalline XIX: mp 184–186° after recrystallization from methanol; mass spectrum, *m/e* 389 (d_1), 2%; *m/e* 390 (d_2), 18%; *m/e* 391 (d_3), 80%.

5α-Cholestan-3β-ol-1,1-d_2 (XXI).—The trideuterio alcohol XIX (52 mg) was dissolved in acetone by gentle warming and treated with Jones[18] reagent until an orange color persisted for 1 min. The reaction mixture was concentrated under reduced pressure, poured into water, and extracted with ether. The ethereal extract was washed with water, 5% sodium bicarbonate, and water and dried over magnesium sulfate. Evaporation of solvent under diminished pressure afforded 50 mg of 5α-cholestan-3-one-1,1-d_2 (XX), which after a recrystallization from methanol exhibited a melting point of 127.5–129°.

5α-Cholestan-3β-ol-1,1-d_2 was prepared by lithium tri-*t*-butoxyaluminum hydride[15] reduction of the corresponding ketone as described above (see preparation of II) and was purified by preparative thin layer chromatography in a 3:1 benzene–ether solvent system. Recrystallization from methanol afforded XXI: mp 143–144.5°; mass spectrum, *m/e* 388 (d_0), 3%; *m/e* 389 (d_1), 16%; *m/e* 390 (d_2), 81%.

Acknowledgment.—The work was performed with financial assistance of the National Institutes of Health, U. S. Public Health Service (Grant No. CA07195).

(21) A. Fürst and P. A. Plattner, *Helv. Chim. Acta*, **32**, 275 (1949).
(22) D. N. Jones and M. A. Saeed, *J. Chem. Soc.*, 4657 (1963).

Synthesis and Stereochemistry of Hydrophenanthrenes. IV. 1,2,3,4,4aα,4bβ,5,6,7,9,10,10aβ-Dodecahydro-4,7-dioxo-2α-phenanthrenecarboxylic Acid[1,2]

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Two synthetic routes leading to the title compound, the racemic *anti–trans* diketo acid IX, are described. Both involve the metal–ammonia reduction of ring A of an octahydrophenanthrene derivative (III or XVII). While the B/C *trans* hydroxy acid XVII could be converted directly to the desired *anti–trans* diketo acid IX, the synthesis from the B/C *cis* hydroxy acid III required the inversion of the 4a-C center. The structural and stereochemical assignments were confirmed by nmr spectroscopy.

In continuation of the work aimed at the synthesis of steroid-like compounds and toward the elucidation of the stereochemistry of hydrophenanthrene derivatives,[4–6] the preparation of the title compound, the racemic *anti–trans* diketo acid IX, is described.

Two synthetic routes have been developed for the preparation of the title compound. One starts with the B/C *cis* keto acid I and the other with the B/C *trans* keto acid XV. The stereochemistry of the starting materials (I and XV) has already been established by chemical means, and by nmr spectroscopy of their respective oximes, II and XVI.[5] The signal of the 4a-hydrogen of II appeared at δ 3.80 (doublet, J = 5.0 cps), whereas the signal of the 4a-hydrogen of XVI is at δ 3.53 (doublet, J = 8.0 cps). This is in agreement with the relationship established between the dihedral angle and the coupling constant of vicinal hydrogens.

The B/C *cis* keto acid I was first reduced with sodium borohydride to the nonlactonizing B/C *cis* hydroxy acid III. This acid III could be oxidized back to the B/C *cis* keto acid I which shows that no change in the configuration occurred during the reduction.[5] The lithium in liquid ammonia reduction of ring A of this hydroxy acid III (rather than the keto acid I) was undertaken to avoid a mixture of stereoisomers at C-4 and C-4a, respectively (see Scheme I).

The use of the original Birch procedure yielded considerable amounts of tetrahydro derivatives with or

(1) Presented before the Organic Chemical Division at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965.
(2) All compounds described in this paper are racemates. As a matter of convenience, only one enantiomeric series (10aβ-hydrogen) has been pictured.
(3) Deceased Feb 17, 1964.
(4) Paper I: Z. G. Hajos, K. J. Doebel, and M. W. Goldberg, *J. Org. Chem.* **29**, 2527 (1964).
(5) Paper II: Z. G. Hajos, D. R. Parrish, and M. W. Goldberg, *ibid.*, **30**, 1213 (1965).
(6) Paper III: Z. G. Hajos, D. R. Parrish, and M. W. Goldberg, *ibid.*, **30**, 2849 (1965).