(*R*)-**6**, 55124-25-9; (±)-**7**, 55124-26-0; (−)-(*S*)-**7**, 55156-08-6; (±)-**8**, 55124-27-1; (−)-(*S*)-**8**, 55156-09-7; (±)-**9**, 55124-28-2; (−)-(*R*)-**9**, 55156-10-0; 2,2-diphenylethanol, 614-29-9; 2,2-diphenylacetic acid, 117-34-0; 2,2-diphenylethyl toluenesulfonate, 6944-27-0; *p*-toluenesulfonyl chloride, 98-59-9; diethyl (2,2-diphenylethyl)methylmalonate, 55124-29-3; diethyl methylmalonate, 609-08-5; ethyl (±)-2-isocyanato-2-methyl-4,4-diphenylbutanoate, 55124-30-6; (±)-2-amino-2-methyl-4,4-diphenylbutanoic acid, 55124-31-7; (±)-2-amino-2-methyl-4,4-diphenylbutanoic acid hydrochloride, 55124-32-8; (−)-menthyl methacrylate, 2231-91-6; methacrylic acid, 79-41-4; phosphorus trichloride, 7719-12-2; methacrylyl chloride, 920-46-7; (−)-*l*-menthol, 2216-51-5; (±)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid, 35389-12-9; (*R*)-1-methyl-2,2-diphenylcyclopropanecarboxylic acid, 4542-84-1; (*R*)-1-methyl-1-trimethylsiloxymethyl-2,2-diphenylcyclopropane, 55124-33-9.

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Synthesis of Stereoisomeric 4-Hydroxymethyl-4-methyl-3β-hydroxycholestanes, -androstanes, and -10-methyl-*trans*-decalins

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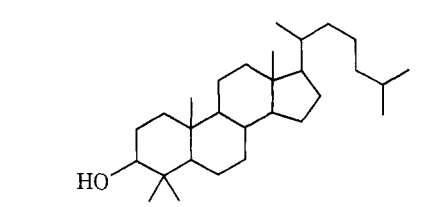
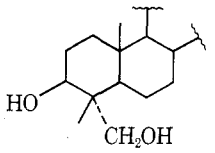
Reductive carbomethoxylation of enones **8**, **9**, and **10** was used as the key step in the preparation of 3β-hydroxycholestanes, 3β-hydroxyandrostanes, and 3β-hydroxy-10β-methyl-*trans*-decalins with 4α-hydroxymethyl-4β-methyl and 4β-hydroxymethyl-4α-methyl substituents (compounds **2**–**7**). Alkylation of the β-keto esters (**11**–**13**) resulting from reductive carbomethoxylations of enones **8**–**10** led to both 4β- and 4α-methyl compounds with the 4β isomer as the major product (~55%) in each case. Stereochemical assignments were made principally on the basis of the shielding effect that a 4β-carbomethoxyl group has on the NMR signal of the 10β-methyl group. Reduction of the methylated β-keto esters led to diols **2**–**7**, which were desired for study as possible intermediates in enzymic oxidative demethylation.

As part of a study of oxidative demethylation at C-4 during steroid biosynthesis,[1-3] we required derivatives of 4,4-dimethylcholestan-3β-ol (**1**) with the 4α or 4β methyl group in various stages of oxidation, particularly 4α-hydroxymethyl and 4β-hydroxymethyl compounds **2** and **3**.[1] The analogous derivatives **4** and **5** in the androstane series and **6** and **7** in the 10-methyl-*trans*-decalin[4] series were also needed for studies intended to determine the effect which substrate truncation would have on the enzymic demethylation process.[5] In this paper the details of the syntheses of these six diols and several related compounds are described.

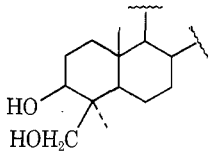
Scheme I shows the pathway used for preparation of each of the three sets of diols. The same approach had been used previously for the synthesis of naturally occurring di-



1

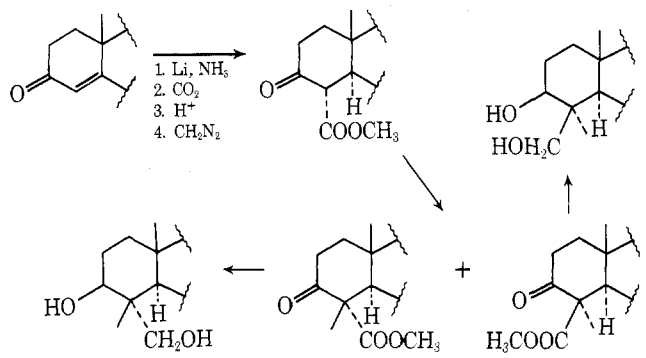


2



3

Scheme I



terpenes of the abietic acid[6-8] and podocarpic acid[9] series. The key step is reductive carbomethoxylation[10] of the appropriate enone followed by methylation of the resulting β-keto esters, which leads in all three cases to both stereoisomers at C-4. After separation and identification, these were reduced to the desired diols.

The requisite starting materials, unsaturated ketones **8**, **9**, and **10** (Scheme II), were prepared by known methods (see Experimental Section). Reductive carbomethoxylation of enone **10** has been reported by Stork[10] to afford β-keto ester **13** as an oil in 34% yield. In our hands a slightly different procedure gave 44% of **13** as an oil from which 37% of pure **13**, mp 60–64°, was obtained. The same procedure applied to **9** afforded 43% of **12**.

With enone **8**, however, the yield of 4α-carbomethoxycholestan-3-one (**11**)[11] from reductive carbomethoxylations never exceeded 33% and was often extremely low. Usually isolated in greater amount was the dimeric substance **14**, produced by reductive coupling.[12] This "cholestenone pinacol" has previously been isolated by a variety of procedures, including electrochemical reduction of **8**.[13,14]

Efforts were made to minimize the formation of **14** by varying reaction conditions. For instance, various nonpolar solvents were added in large amounts to test the hypothesis that the undesired reductive coupling was being promoted by a tendency for the fatty **8** to be associated with itself in liquid ammonia. These experiments failed, and the reasons why **14** tends to form remains obscure. However, even taking into account the low yield (typically around 20%), reductive carbomethoxylation of **8** is more convenient than the previous preparation of **11**.[11]

Certain C-4 monosubstituted steroids were also needed for our biochemical studies,[2] so some β-keto ester from each series was reduced rather than methylated. Since β-keto esters **11–13** were, as expected,[15,7] completely nonenolic, reduction to diol could be effected without difficulty using lithium aluminum hydride. It was anticipated[16] that a preponderance of the desired equatorial alcohol **15** would be formed. However, $LiAlH_4$ reduction of **11** afforded the 3α isomer **16** and **15** in approximately a 2:1 ratio. Assignment of stereochemistry at C-3 was made on the basis of the NMR spectra of the diacetates derived from **15** and **16**, which showed the expected differences between the C-3 protons bonded to carbons bearing equatorial and axial acetoxyl groups, respectively.[17]

In an effort to obtain a greater proportion of the desired diols **17** and **18** in the other two series, reduction of β-keto esters **12** and **13** was tried with sodium borohydride, despite the fact that $NaBH_4$ usually affords a larger fraction of axial alcohol than $LiAlH_4$.[18] As it turned out, 3β-hydroxy esters **19** and **20** were obtained as the dominant products (ca. 65% crude yield) from $NaBH_4$ reduction of **12** and **13**. These in turn were reduced with $LiAlH_4$ to **17** and **18**. Consistent with these results was $NaBH_4$ reduction of **11**, which afforded 65% of a hydroxy ester convertible to **15** by treatment with $LiAlH_4$ and 20% of a hydroxy ester convertible to **16**. No further exploration was made of the interesting effect that the 4α-carbomethoxyl group has on the stereochemical course of the $LiAlH_4$ reduction of **11**.

Table I
NMR Chemical Shifts (δ, $CDCl_3$) of Methyl Group Singlets in Seven Pairs of Isomers with Methyl and Carbomethoxyl Groups at C-4

Compound	C-18	10β-CH_3	4α-CH_3	4β-CH_3	-$COOCH_3$
21	0.67	1.06		1.35	3.68
22	0.66	0.97	1.32		3.65
23	0.65	0.90		1.15	3.64
24	0.64	0.69	1.18		3.62
25	0.73	1.08		1.37	3.70
26	0.70	0.96	1.26		3.62
27		1.10		1.25	3.70
28		0.99	1.26		3.61
37	0.65	0.87		1.16	3.70
38	0.65	0.71	1.40		3.62
39	0.70	0.90		1.14	3.75
40	0.70	0.74	1.37		3.72
41		0.95		1.10	3.66
42		0.75	1.35		3.70

Methylation of β-keto esters **11–13** was accomplished by treatment with sodium hydride and a trace of *tert*-butyl alcohol in dimethoxyethane, followed by methyl iodide.[7] From **11** there was obtained after chromatography 56% of the 4β-methylated compound **21** and 19% of 4α-methylated **22**. The stereochemical assignments to **21** and **22** were based on the previously documented fact[7,19] that an axial carbomethoxyl group at C-4, as in **22**, causes the NMR signal of the 10β-methyl group to be shifted upfield. In Table I are compiled the pertinent data on the seven pairs of compounds prepared in this study for which this shielding effect is evident in the 4β-carbomethoxy isomer.

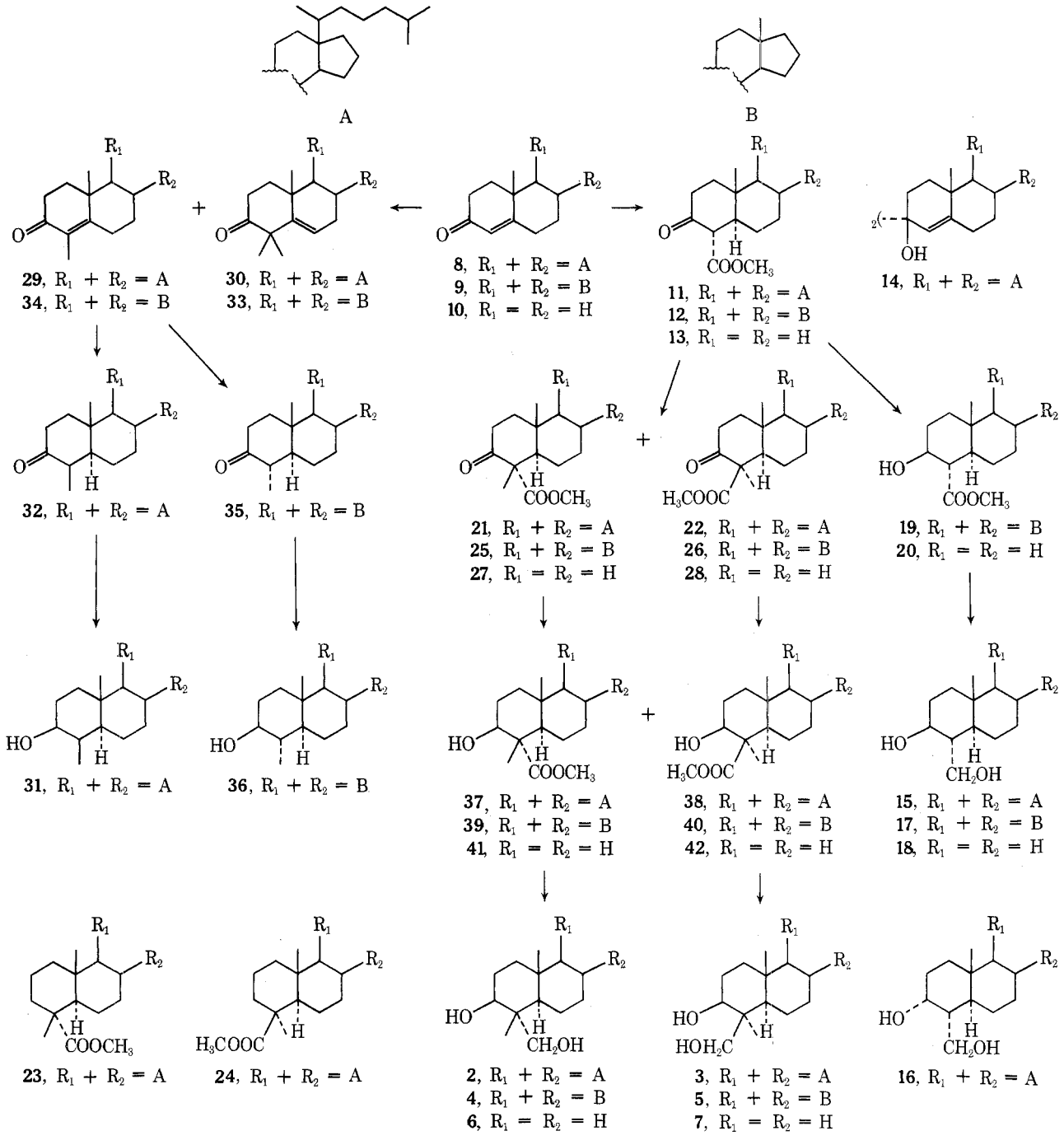
It had been previously noticed[7] that compounds which lacked the C-3 carbonyl group exhibited a considerably enhanced shielding of the angular methyl group by a 4β-carbomethoxyl. To see if this would also be observed in the cholestane series, **21** and **22** were subjected to Clemmensen reduction conditions of Wenkert.[20] The product from the Clemmensen reduction of **21** was contaminated with a large amount of unsaturated material[21] (NMR vinyl proton absorption) but pure **23** was obtained by hydrogenation of the mixture. Clemmensen reduction of **22** gave **24** directly. The expected enhanced shielding in **24** (0.21 ppm vs. 0.09 ppm in **22**) was indeed observed, in confirmation of the stereochemical assignments.[22]

Methylation of the β-keto esters in the androstane and decalin series proceeded analogously. From **12** was obtained 54% of **25** and 33% of **26**; from **13**, 56% of **27** and 28% of **28**. The preference for β alkylation in all three cases was expected on the basis of previous work,[7,20] and the β:α ratio was roughly the same in all cases.

Similar alkylations were performed on enones **8** and **9**. Methylation of **8** was conducted by the procedure of Atwater[23] to afford a separable mixture of **29** and **30**. Monomethylated **29** was converted to 4β-methylcholestan-3β-ol (**31**) by hydrogenation to **32**,[24] followed by reduction with lithium *tri-tert*-butoxyaluminum hydride.[25] Methylation of **9** gave the known[26] **33** and the monomethylated **34**, mp 100–103°. Lithium–ammonia reduction of **34** yielded **35**, which was converted to **36** by sodium borohydride.

The desired diols **2–7** were readily obtained from the methylated β-keto esters. Treatment of **21**, **22**, and **25–28**

Scheme II



with $NaBH_4$ led to the corresponding 3β-hydroxy esters **37–42**. Assignment of the β configuration to the hydroxyl group in each of these substances was made by NMR.[17] Finally, treatment of each hydroxy ester with $LiAlH_4$ led to diol: **37** → **2**, mp 219–220°; **38** → **3**, mp 209–210°; **39** → **4**, mp 203–204°; **40** → **5**, mp 143–144°; **41** → the previously reported[27] **6**, mp 97–98°; and **42** → **7**, an oil.

Experimental Section

Melting points were determined in open capillaries using a Thomas-Hoover apparatus and are uncorrected. Unless otherwise specified, ir spectra of solids were obtained as KBr pellets and liquids as neat films on a Perkin-Elmer 137 spectrophotometer. Unless otherwise specified, NMR spectra were determined in $CDCl_3$ on a Perkin-Elmer R-24 spectrometer with Me_4Si as an internal standard. Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. Preparative TLC was performed on 20 × 20 cm plates coated with 1.45-mm thick layers of silica gel $PF_{254+366}$ (Brinkmann Instruments, Inc., Westbury, N.Y.) which had been mixed with 0.002% Rhodamine 6G dye (Eastman Kodak Co., Rochester, N.Y.). Uv light was used to visualize TLC plates. Brine refers to saturated aqueous sodium chloride solution.

4α-Carbomethoxycholestan-3-one (11). To a 2-l., three-necked flask, equipped with a mechanical stirrer and a reflux condenser, was added 800 ml of liquid ammonia followed by 1.12 g (0.16 mol) of lithium wire which had been cut into 1-cm lengths and washed with hexane to remove mineral oil. The resulting blue mixture was stirred for 15 min and a solution of 15.39 g (0.040 mol) of Δ^4-cholesten-3-one[28] (**8**) in 200 ml of anhydrous ether was added over a 1-hr period while vigorous stirring was maintained. The mixture was stirred for another 1 hr and then a steam bath was applied to the flask to speed evaporation of the ammonia. When the coating of ice on the flask melted, 600 ml of anhydrous ether was added and a Drierite tube was attached to the condenser. The mixture was refluxed for 30 min to drive off any residual ammonia and then was cooled to Dry Ice–acetone temperature.

During this cooling period a piece of Dry Ice (ca. 50 g) was pul-

verized in a cloth bag enclosed in a plastic bag. This fine powder was then added to the cold reaction mixture through a powder funnel which was also encased in a larger plastic bag. Care was taken to exclude moisture. The reaction flask was removed from the cooling bath and stirred for 30 min, and then was placed in a room-temperature water bath and stirred for 30 min. The mixture was cooled again in a Dry Ice–acetone bath and 100 g of powdered Dry Ice was added, followed by slow addition of 30 ml of 95% ethanol (to destroy excess lithium metal) and 200 ml of cold water. The contents of the flask were cooled to −10° under nitrogen and 20% hydrochloric acid was added until the reaction mixture was acidic. The mixture was quickly transferred to a separatory funnel which contained ice. The aqueous layer was separated and washed once with ether. The combined organic layers were washed once with cold brine and then added dropwise to a rapidly stirred solution of excess, freshly distilled diazomethane in ether at −78°. After 2 hr the excess diazomethane was destroyed by careful addition of acetic acid, and the mixture was concentrated in vacuo. The residue was dissolved in 400 ml of hexane and cooled to 0° for 4 hr. During this time a precipitate formed which was collected by filtration and washed with hexane to afford 3.4 g (22%) of **14**. Two recrystallizations from hexane gave an analytical sample: mp 215–217° (lit.[14] mp 225–227°); ir 3400 cm^{-1}; NMR δ 2.50 (s, HO–) and 5.25 ppm (s, HC≡C–); M^+ *m/e* 770.

Anal. Calcd for $C_{54}H_{90}O_2$: C, 84.09; H, 11.76. Found: C, 83.79; H, 11.88.

The hexane filtrate was evaporated and the residue was dissolved in 100 ml of ether and stored at −10° for 48 hr. During this time a precipitate formed which was collected by filtration and washed with a small amount of cold ether to afford 3.66 g (21%) of **11**. Recrystallization from ether afforded 3.02 g (17%) of **11**: mp 170–172° (lit.[11] mp 170–172°); ir 1740 and 1720 cm^{-1} [lit.[11] ir (Nujol) 1740 and 1710 cm^{-1}]; NMR δ 0.67 (s, H_3C_{18}–), 1.03 (s, 10 β-H_3C–), 3.23 (d, J = 12 Hz, 4β-H), and 3.73 ppm (s, H_3COOC–). The yield of **11** varied from 0 to 33%. It was often necessary to use column chromatography (elution with 9:1 hexane–ether from acid-washed alumina) to isolate pure **11**.

Concentration of the ethereal filtrate afforded 8.15 g of a solid mixture of **8**, cholestan-3-one, and a trace of **11**.

4α-Carbomethoxyandrostan-3-one (12). Reductive carbomethoxylation of **9** was conducted by the following, simpler procedure. Into an oven-dried 500-ml three-necked flask, equipped with a Dewar condenser, a glass paddle mechanical stirrer, and a dropping funnel, was placed 200 ml of liquid ammonia and 150 mg (0.0214 mol) of lithium wire which had been wiped witlh a hexane-soaked cloth. The resulting blue mixture was stirred for 1 hr and a solution of 1.000 g (0.0037 mol) of **9**,[29] which had been dried in vacuo at 78° for 48 hr, in 15 ml of dry tetrahydrofuran was added dropwise rapidly. Vigorous stirring was continued for 1 hr. The ammonia was evaporated with a warm water bath and 75 ml of dry ether was added. The mixture was then refluxed for 30 min to ensure evaporation of any residual ammonia. The system was cooled and ca. 200 g (4.5 mol) of pulverized Dry Ice (taken from the center portion of a 50-lb block) was rapidly added. The slurry was stirred vigorously until it warmed to −10° (ca. 2 hr). Large pieces of residual lithium were removed with tweezers and then cold 10% sulfuric acid was added dropwise until the mixture became homogeneous (pH ~2). The solution was poured into a separatory funnel and quickly washed with two 50-ml portions of brine. The ethereal layer was dripped into cold excess ethereal diazomethane with stirring. The excess diazomethane was removed by blowing a stream of nitrogen into the flask; the resulting organic layer was dried ($MgSO_4$) and concentrated in vacuo to give 1.22 g of a crude yellow solid. This was distributed among five preparative TLC plates which were developed four times with 4:1 hexane–ether. Elution of the fastest moving band gave 0.178 g (18%) of androstan-3-one. The next band gave 0.390 g (43%) of **12**. The third band gave 0.250 g of **9**; the fourth band gave 0.048 g (5%) of androstan-3β-ol. The last band afforded 0.114 g (6%) of polar material which was recrystallized from 1:1 methanol–chloroform to give a substance with mp 225–230°; ir (KBr) 3400 cm^{-1}; NMR δ 5.62 ppm (br s, vinyl H). This material, thought to be the dimeric diol analogous to **14**, was not characterized further.

Recrystallization of **12** from ether afforded 0.300 g (25%) of white cubes: mp 160–162°; ir 1745 and 1710 cm^{-1}; NMR δ 0.69 (s, 3, H_3C_{18}–), 1.01 (s, 3, 10β-H_3C–), 3.22 (d, 1, J = 15 Hz, 4β-H), and 3.69 ppm (s, 3, H_3COOC–).

Anal. Calcd for $C_{21}H_{32}O_3$: C, 75.86; H, 9.70. Found: C, 75.91; H, 9.73.

4α-Carbomethoxy-10β-methyl-*trans*-decal-3-one (13). Reductive carbomethoxylation of enone **10**[30] was carried out in the same manner as that of **9**, which differs slightly from the published procedure for this conversion.[10] From 10.000 g (0.0610 mol) of **10** there was obtained 11.031 g of crude product which was chromatographed on 500 g of silica gel activated at 110° for 5 hr. Elution with 1:10 ether–petroleum ether (bp 37–48°) gave 0.514 g (4%) of 2α-carbomethoxy-10β-methyl-*trans*-decal-3-one;[31] elution with 1:4 ether–petroleum ether gave 5.918 g (44%) of **13**, followed by 0.685 g of **10**.

The semisolid **13** was recrystallized thrice from hexane to afford 4.992 g (37%) of pure **13**: mp 60–64°; ir 1745 and 1705 cm^{-1}; NMR δ 1.1 (s, 3, 10β-H_3C–), 3.16 (d, 1, J = 11 Hz, 4β-H), and 3.75 ppm (s, 3, H_3COOC–).

Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.72; H, 8.88.

4α-Hydroxymethylcholestan-3β-ol (15) and 4α-Hydroxymethylcholestan-3α-ol (16). To a stirred suspension of 0.19 g (0.005 mol) of $LiAlH_4$ in 20 ml of dry tetrahydrofuran (distilled from $LiAlH_4$), a solution of 0.675 g (0.0015 mol) of **11** in 25 ml of dry tetrahydrofuran was added over a period of 10 min. The mixture was heated at reflux for 1.5 hr and cooled, and ice and dilute sulfuric acid were added. It was then partitioned between 50 ml of water and ether. The ether extracts were washed with water, dilute $NaHCO_3$ solution, and brine, dried over $MgSO_4$, and evaporated to afford 0.670 g of white, crystalline material, mp 207–215°, which TLC (ether) indicated was a mixture of two compounds. This product was chromatographed over 125 g of Merck acid-washed alumina. Elution with ether removed pale yellow gummy material. Elution with ethyl acetate afforded 0.234 g (39%) of **16**, which was recrystallized successively from ether and methanol to give an analytical sample: mp 195–197°; ir 3320 cm^{-1}. NMR data were determined on the crude diacetate of **16** prepared by treatment with acetic anhydride in pyridine at room temperature for 24 hr: δ 2.00 (s, H_3CCOO–), 2.02 (s, H_3CCOO–), 4.05 (br m, $-H_2COOCCH_3$), and 5.13 ppm (br s, 3β-H).

Anal. Calcd for $C_{28}H_{50}O_2$: C, 80.32; H, 12.04. Found: C, 80.41; H, 12.26.

Elution with 9:1 ethyl acetate–methanol afforded 0.160 g (17%) of **15**, which was recrystallized from ether to give material with mp 228–231°, and then from methanol to give an analytical sample: mp 211–213°; ir 3240 cm^{-1}. NMR data were determined on the crude diacetate of **15** prepared in the same manner: δ 2.02 (s, 2 H_3CCOO–), 4.08 (br s, $-H_2COOCCH_3$), and 4.65 ppm (br m, 3α-H).

Anal. Calcd for $C_{28}H_{50}O_2$: C, 80.32; H, 12.04. Found: C, 80.01; H, 12.01.

Preparative TLC using 3:2 hexane–ether twice of the product from another $LiAlH_4$ reduction of **11** afforded 54% of **16** and 27% of **15**. Reduction of 0.200 g (0.45 mmol) of **11** with $NaBH_4$ as described below for **12** afforded, after preprative TLC using 2:1 hexane–ether twice, 0.039 g (20%) of a hydroxy ester (ir 3550 and 1730 cm^{-1}) which was converted exclusively to **16** by $LiAlH_4$, and 0.130 g (65%) of a hydroxy ester (ir 3450 and 1725 cm^{-1}) which was converted exclusively to **15** by $LiAlH_4$.

4α-Carbomethoxyandrostan-3β-ol (19). A mixture of 0.100 g (0.3 mmol) of **12**, 0.010 g (0.26 mmol) of $NaBH_4$, and 10 ml of methanol was stirred for 2 hr at room temperature. The methanol was evaporated in vacuo and the resulting solid was partitioned between 25 ml of ether and 10 ml of 5% sulfuric acid. The ether layer was separated, dried ($MgSO_4$), and concentrated in vacuo to give 0.110 g from which preparative TLC, using 1:1 ether–hexane twice, afforded 0.040 g of material presumed to be crude 4α-carbomethoxyandrostan-3α-ol on the basis of its NMR spectrum [δ 3.65 (s, 3, H_3COOC–) and 4.05 ppm (br s, 3β-H)], 0.064 g (63%) of crude **19**, and 0.002 g of polar material, presumably diol. Recrystallization of **19** from isopropyl alcohol afforded 0.039 g (38%) of white, silky crystals: mp 173–174°; ir 3300 and 1740 cm^{-1}; NMR δ 0.67 (s, 3, H_3C_{18}–), 0.82 (s, 3, 10β-H_3C–), 3.70 (s, 3, H_3COOC–), and 3.5–3.8 ppm (m, 2, 4β-H and 3α-H).

Anal. Calcd for $C_{21}H_{34}O_3$: C, 75.41; H, 10.25. Found: C, 75.45; H, 10.32.

4α-Carbomethoxy-10β-methyl-*trans*-decal-3β-ol (20). Reduction of 0.400 g (1.8 mmol) of **13** with $NaBH_4$ in exactly the same manner as **12** afforded 0.120 g of material presumed to be crude 4α-carbomethoxy-10β-methyl-*trans*-decal-3α-ol on the basis of its NMR spectrum [δ 3.51 (br s, 4β-H), 3.65 (s, 3, H_3COOC–), and 4.11 ppm (br s, 3β-H)], 0.281 g (69%) of oily **20**, and 0.023 g of polar material, presumably diol. Purification of **20** was effected by sublimation twice at 63° (65 mm) to afford 0.183 g (48%) of **20** as white, silky crystals: mp 69°; ir 3400 and 1735 cm^{-1}; NMR δ 0.91

(s, 3, 10β-H_3C–) and 3.5–4.0 ppm (m and s overlapping, 5, H_3COOC–, 3α-H and 4β-H).

Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.79. Found: C, 69.08; H, 9.77.

4α-Hydroxymethylandrostan-3β-ol (17). A mixture of 0.066 g (0.19 mmol) of **19**, 0.020 g (0.52 mmol) of $LiAlH_4$, and 10 ml of ether was stirred for 2 hr at room temperature. Excess $LiAlH_4$ was destroyed with 2 drops of ethyl acetate followed by 5 ml of 10% sulfuric acid. Standard work-up with ether and concentration in vacuo afforded 0.042 g of a white solid, which was recrystallized from ether to give 0.027 g (46%) of pure **17** as white plates: mp 194–196°; ir ($CHCl_3$) 3300 cm^{-1}; NMR δ 0.70 (s, 3, H_3C_{18}–), 0.90 (s, 3, 10β-H_3C–), and 3.0–4.5 ppm (m, 5).

Anal. Calcd for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18. Found: C, 78.20; H, 11.10.

4α-Hydroxymethyl-10β-methyl-*trans*-decal-3β-ol (18). Reduction of 0.073 g (0.32 mmol) of **20** with $LiAlH_4$ in exactly the same manner as **19** afforded 0.081 g of a crude product which was sublimed at 100° (15 mm) to give 0.056 g (88%) of **18** as white plates: mp 117–118°; ir 3300 cm^{-1}; NMR δ 0.88 (s, 3, 10β-H_3C–) and 3.4–4.2 ppm (m, 5).

Anal. Calcd for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.72; H, 11.09.

4α-Carbomethoxy-4β-methylcholestan-3-one (21) and 4β-Carbomethoxy-4α-methylcholestan-3-one (22). To a stirred solution of 1.51 g (3.4 mmol) of keto ester **11** in 100 ml of dimethoxyethane, which had been distilled from sodium and redistilled from $LiAlH_4$, was added 0.35 g (4.2 mmol) of NaH (55% dispersion in mineral oil) and 8 drops of dry *tert*-butyl alcohol under a nitrogen atmosphere. After the evolution of gas ceased, 19.4 g (8.5 ml, 0.13 mol) of methyl iodide was added and the mixture was heated at 70° for 4 hr and at 85° for 1 hr. The mixture was cooled, diluted with 15 ml of cold water, concentrated to a volume of ca. 50 ml in vacuo, diluted with water, and extracted with ether. The ether extracts were washed with water and brine, dried ($MgSO_4$), and evaporated to afford 1.87 g of pale yellow oil which was chromatographed on 130 g of acid-washed alumina. Elution with hexane removed mineral oil (0.27 g). Elution with 9:1 hexane–ether afforded 0.29 g (19%) of **22**, mp 110–111°. Recrystallization from methanol afforded an analytical sample as needles: mp 117–118°; ir 1740 and 1720 cm^{-1}; NMR δ 0.66 (s, H_3C_{18}–), 0.97 (s, 10β-H_3C–), 1.32 (s, 4α-H_3C–), and 3.65 ppm (s, H_3COOC–).

Anal. Calcd for $C_{30}H_{50}O_3$: C, 78.55; H, 10.99. Found: C, 78.54; H, 10.91.

Further elution with 5:1 hexane–ether afforded 0.854 g (56%) of **21**, mp 95–96°. Recrystallization from methanol afforded an analytical sample as small plates: mp 100–101°; ir 1745 and 1720 cm^{-1}; NMR δ 0.67 (s, H_3C_{18}–), 1.06 (s, 10β-H_3C–), 1.35 (s, 4β-H_3C–), and 3.68 ppm (s, H_3COOC–).

Anal. Calcd for $C_{30}H_{50}O_3$: C, 78.55; H, 10.99. Found: C, 78.52; H, 10.93.

4α-Carbomethoxy-4β-methylandrostan-3-one (25) and 4β-Carbomethoxy-4α-methylandrostan-3-one (26). To a stirred solution of 0.250 g (0.75 mmol) of **12** in 30 ml of dimethoxyethane was added 1 drop of *tert*-butyl alcohol and 0.033 g (0.78 mmol) of sodium hydride (57% dispersion in mineral oil). This mixture was heated at reflux for 2 hr and then a solution of 0.226 g (1.6 mmol) of methyl iodide in 10 ml of dimethoxyethane was dripped in over 30 min. The resulting mixture was stirred at reflux for an additional 3 hr, cooled, and poured into a mixture of 50 ml of ether and 20 ml of water. The aqueous layer was reextracted with 10 ml of ether and the combined organic layers were washed once with 20 ml of 10% HCl and once with 20 ml of water, dried ($MgSO_4$), and evaporated in vacuo to give 0.307 g of a white solid. Preparative TLC, using 4:1 hexane–ether, afforded 0.006 g (2%) of overalkylated material, 0.085 g (33%) of **26**, 0.140 g (54%) of **25**, and 0.042 g (12%) of **12**.

Recrystallization twice from methanol gave 0.042 g (16%) of pure **26**: mp 128–129°; ir 1730 and 1705 cm^{-1}; NMR δ 0.70 (s, 3, H_3C_{18}–), 0.96 (s, 3, 10β-H_3C–), 1.26 (s, 3, 4α-H_3C–), and 3.62 ppm (s, 3, H_3COOC–).

Anal. Calcd for $C_{22}H_{34}O_3$: C, 76.25; H, 9.89. Found: C, 76.19; H, 9.80.

Recrystallization twice from ether gave 0.093 g (36%) of pure **25**: mp 146–147°; ir 1740 and 1705 cm^{-1}; NMR δ 0.73 (s, 3, H_3C_{18}–), 1.08 (s, 3, 10β-H_3C–), 1.37 (s, 3, 4β-H_3C–), and 3.70 ppm (s, 3, H_3COOC–).

Anal. Calcd for $C_{22}H_{34}O_3$: C, 76.25; H, 9.89. Found: C, 76.31; H, 9.73.

4α-Carbomethoxy-4β,10β-dimethyl-*trans*-decal-3-one (27) and 4β-Carbomethoxy-4α,10β-dimethyl-*trans*-decal-3-one (28). Methylation of β-keto ester **13** was conducted in exactly the same manner as methylation of **12**, except that tlhe reaction was allowed to proceed for an additional 1 hr. The same work-up afforded, from 0.500 g (2.2 mmol) of **13**, 0.673 g of crude product, which upon preparative TLC using 4:1 hexane–ether afforded 0.019 g (3.6% based on 518 mg of recovered material) of overalkylated material which was not characterized, 0.146 g (28%) of **28**, 0.289 g (55%) of **27**, and 0.064 g (12%) of **13**.

Compound **28** was purified by preparative TLC using 4:1 hexane–ether to an oil which was homogeneous by TLC: ir 1735 and 1710 cm^{-1}; NMR δ 0.99 (s, 3, 10β-H_3C–), 1.26 (s, 3, 4α-H_3C–), and 3.61 ppm (s, 3, 4β-H_3COOC–); M^+ *m/e* 238.1571 (calcd for $C_{14}H_{22}O_3$, 238.1568).

Compound **27** was purified by preparative TLC using 4:1 hexane–ether to an oil which was homogeneous by TLC: ir 1745 and 1705 cm^{-1}; NMR δ 1.10 (s, 3, 10β-H_3C–), 1.25 (s, 3, 4β-H_3C–), and 3.70 ppm (s, 3, H_3COOC–); M^+ *m/e* 238.1569 (calcd for $C_{14}H_{22}O_3$, 238.1568).

4α-Carbomethoxy-4β-methylcholestane (23). According to a Clemmensen reduction procedure reported by Wenkert,[20] a suspension of amalgamated zinc (prepared by shaking 9.0 g of zinc moss in a solution of 0.6 g of mercuric chloride and 0.5 ml of concentrated hydrochloric acid in 6 ml of water for 15 min, and then washing the undissolved zinc with water) and 0.28 g (0.61 mmol) of **21**, mp 101–102°, in 6 ml of 15% hydrochloric acid was refluxed for 60 hr. During this time 0.5 ml of concentrated hydrochloric acid was added to the reaction mixture every 8 hr. The cooled mixture was extracted with ether. The organic layer was washed with water, sodium bicarbonate solution, and brine, dried ($MgSO_4$), and evaporated to give 0.27 g of a viscous oil. The crude oil was purified by preparative TLC, using 9:1 hexane–ether, to give 0.23 g of crystalline material. Recrystallization from ethanol afforded 0.16 g: mp 73–78°; ir 1740 cm^{-1}; NMR δ 5.5 ppm (m);[21] TLC on silica gel G impregnated with 12% $AgNO_3$, using 19:1 hexane–ether, showed two components; GLC (Varian 2100 instrument, 3% QF-1, 6 ft × 4 mm column, 220°) indicated (disc chart integration) the mixture to be 1.6 parts **23** to 1 part presumably unsaturated material.

The entire 0.23 g of crystalline product was hydrogenated over 0.08 g of 10% Pd/C in 85 ml of ethanol for 1.5 hr at atmospheric pressure. The catalyst was removed by filtration and the filtrate was evaporated to give 0.21 g of a white solid which TLC and GLC indicated was homogeneous. Recrystallization from ethanol afforded 0.17 g (63% from **21**) of **23**, mp 80–82°. Further recrystallizatiorn from ethanol afforded an analytical sample: mp 81–82.5°; ir 1740 cm^{-1}; NMR δ 0.65 (s, H_3C_{18}–), 0.90 (s, 10β-H_3C–), 1.15 (s, 4β-H_3C–), and 3.62 ppm (s, H_3COOC–).

Anal. Calcd for $C_{30}H_{52}O_2$: C, 81.02; H, 11.79. Found: C, 81.13; H, 11.78.

4β-Carbomethoxy-4α-methylcholestane (24). Exactly as in the preparation of **23** from **21**, 0.080 g (0.17 mmol) of **22**, mp 115–116°, was subjected to Clemmensen reduction. There was obtained 0.077 g of solid, mp 70–78°. One recrystallization from hexane gave 0.066 g (84%) of **24**: mp 78–80°; NMR, no vinyl proton absorption. Further recrystallization from hexane afforded an analytical sample: mp 79.5–80.5°; ir 1740 cm^{-1}; NMR δ 0.64 (s, H_3C_{18}–), 0.69 (s, 10β-H_3C–), 1.18 (s, 4α-H_3C–), and 3.62 ppm (s, H_3COOC–).

Anal. Calcd for $C_{30}H_{52}O_2$: C, 81.02; H, 11.79. Found: C, 81.33; H, 11.86.

4β-Methylcholestan-3β-ol (31). To a stirred solution of 0.500 g (1.29 mmol) of 4β-methylcholestan-3-one (**32**)[24] in 25 ml of dry tetrahydrofuran at 0° was added, dropwise, a slurry of 1.50 g of lithium tri-*tert*-butoxyaluminum hydride in 40 ml of tetrahydrofuran. This mixture was stirred at 0° for 2 hr and at room temperature for 2 hr. It was then acidified with dilute hydrochloric acid, concentrated in vacuo, and extracted with ether. The organic layer was washed with water, dried ($MgSO_4$), and evaporated to give 0.490 g (98%) of **31**, mp 157–161°. Recrystallization from methanol afforded an analytical sample, mp 160.5–162.5°,[25] ir 3360 cm^{-1}.

Anal. Calcd for $C_{28}H_{50}O$: C, 83.51; H, 12.51. Found: C, 83.65; H, 12.47.

4-Methyl-Δ⁴-androsten-3-one (34). To a mixture of 70 ml of dry *tert*-butyl alcohol and 0.500 g (11 mmol) of NaH (57% dispersion in mineral oil), under nitrogen, was added 2.00 g (7.3 mmol) of **9**. The resulting mixture was refluxed for 1 hr and then a solution of 1.50 g (10.5 mmol) of methyl iodide in 10 ml of dry *tert*-butyl alcohol was added dropwise over 30 min. After being refluxed for an additional 1 hr, the mixture was cooled and evaporated in vacuo. The resulting yellow gum was dissolved in 150 ml of ether and washed with two 50-ml portions of 5% sulfuric acid and two 50-ml

portions of water. The organic layer was dried ($MgSO_4$) and evaporated in vacuo to give 2.9 g of a yellow solid, which was chromatographed on 60 g of silica gel in hexane. Elution with ether–hexane gave 0.657 g (30%) of **33**. Recrystallization from acetone afforded 0.432 g (20%) of pure **33**: mp 174–175° (lit.[26] mp 178–180°); ir 1705 cm^{-1}; NMR δ 0.71 (s, 3, H_3C_{18}–), 0.85 (s, 3, 10β-H_3C–), 1.22 (s, 6, 4α- and 4β-H_3C–), and 5.55 ppm (m, 1, 6-H).

Next eluted was 0.808 g of solid which was recrystallized from methanol to give 0.583 g (28%) of pure **34**: mp 100–103°; ir 1675 cm^{-1}; NMR δ 0.85 (s, 3, H_3C_{18}–), 1.24 (s, 3, 10β-H_3C–), and 1.88 ppm (s, 3, 4 H_3C–).

Anal. Calcd for $C_{20}H_{30}O$: C, 83.85; H, 10.55. Found: C, 83.76; H, 10.43.

Further elution afforded 0.489 g of **9**.

4α-Methylandrostan-3-one (35). To a 100-ml three-necked flask equipped with a Dewar condenser, an addition funnel, and a glass paddle mechanical stirrer was added 55 ml of liquid ammonia and 0.055 g (7.8 mmol) of lithium wire which had been wiped with a hexane-soaked cloth. After this blue mixture had been stirred for 30 min, a solution of 0.400 g (1.4 mmol) of **34** in 15 ml of ether was added rapidly and stirring was continued for 10 min. The ammonia was evaporated with the aid of a warm water bath and 30 ml of ether, 5 ml of 95% ethanol, and 5 ml of water were added. This solution, plus an additional 30 ml of ether, was poured into 50 ml of water. The aqueous layer was extracted with 3 × 20 ml of ether and the combined extracts were washed with 30 ml of water, dried ($MgSO_4$), and evaporated in vacuo to give 0.390 g of white solid. This material was dissolved in 25 ml of acetone and oxidized with 1 ml of Jones reagent.[32] A standard ether work-up gave 0.373 g of white solid, which was chromatographed on 15 g of silica gel. Elution with hexane containing increasing amounts of ether afforded **35**, which was recrystallized twice from 95% ethanol to afford 0.164 g (41%) of **35** as white plates: mp 130–132°; ir 1710 cm^{-1}; NMR δ 0.80 (s, 3, H_3C_{18}–), 1.00 (s, 3, 10β-H_3C–), and 1.12 ppm (d, 3, J = 6 Hz, 4α-H_3C–).

Anal. Calcd for $C_{20}H_{32}O$: C, 83.27; H, 11.18. Found: C, 83.18; H, 11.15.

Further elution afforded 0.110 g of **34**.

4α-Methylandrostan-3β-ol (36). A mixture of 0.130 g (0.45 mmol) of **35**, 40 ml of methanol, and 0.050 g (1.3 mmol) of $NaBH_4$ was stirred at room temperature while the disappearance of **35** was monitored by TLC. After 1 hr, the reaction mixture was worked up as in the preparation of **19** to afford 0.140 g of white solid which was purified by preparative TLC using 3:1 hexane–ether. Two substances were eluted. The first, 0.006 g (5%), is tentatively identified as 4α-methylandrostan-3α-ol: mp 147–151°; NMR δ 0.70 (s, 3, H_3C_{18}–), 0.80 (s, 3, 10β-H_3C–), 0.95 (d, 3, J = 4 Hz, 4α-H_3C–), and 3.7 ppm (br s, 1, 3β-H). The second was recrystallized twice from 3:1 methanol–water to afford 0.040 g (31%) of **36**: mp 158–160°; ir 3400 cm^{-1}; NMR δ 0.69 (s, 3, H_3C_{18}–), 0.85 (s, 3, 10β-H_3C–), 1.0 (d, 3, J = 6 Hz, 4α-H_3C–), and 2.9–3.4 ppm (br m, 1, 3α-H).

Anal. Calcd for $C_{20}H_{34}O$: C, 82.69; H, 11.79. Found: C, 82.58; H, 11.82.

4α-Carbomethoxy-4β-methylcholestan-3β-ol (37). Reduction of 0.400 g (0.87 mmol) of **21** with $NaBH_4$ was performed in exactly the same manner as **12**, except that the reaction was allowed to proceed for 12 hr, to afford 0.430 g of crude product which was recrystallized from methanol to give 0.357 g (89%) of **37**, mp 171–173°. Further recrystallization from methanol gave an analytical sample as white needles: mp 173–173.5°; ir 3500 and 1720 cm^{-1}; NMR δ 0.65 (s, H_3C_{18}–), 0.81 (s, 10β-H_3C–), 1.16 (s, 4β-H_3C–), 3.70 (s, H_3COOC–), and 3.9–4.1 ppm (br m, 3α-H).

Anal. Calcd for $C_{30}H_{52}O_3$: C, 78.21; H, 11.38. Found: C, 78.33; H, 11.42.

4β-Carbomethoxy-4α-methylcholestan-3β-ol (38). Reduction of 0.286 g (0.62 mmol) of **22** with $NaBH_4$ in exactly the same manner as **12** except that the reaction was allowed to proceed for 12 hr afforded 0.278 g of crude product which was recrystallized from ether to give 0.211 g (74%) of **38**, mp 145–147°. Further recrystallization from ether gave an analytical sample: mp 147–148°; ir 3550 and 1700 cm^{-1}; NMR 0.65 (s, H_3C_{18}–), 0.71 (s, 10β-H_3C–), 1.40 (s, 4α-H_3C–), 2.75–3.50 (br m, 3α-H), and 3.62 ppm (s, H_3COOC–).

Anal. Calcd for $C_{30}H_{52}O_3$: C, 78.21; H, 11.38. Found: C, 78.29; H, 11.47.

4α-Carbomethoxy-4β-methylandrostan-3β-ol (39). Reduction of 0.050 g (0.14 mmol) of **25** with $NaBH_4$ in exactly the same manner as **12** afforded 0.055 g of crude product which was purified by preparative TLC, using 1:1 hexane–ether twice, to afford 0.008 g (16%) of material tentatively identified as 4α-carbomethoxy-4β-methylandrostan-3α-ol, 0.039 g (78%) of **39**, and 4 mg of polar material, presumably diol. Recrystallization of **39** from ether afforded 0.022 g (45%) of white cubes: mp 188–189°; ir 3700 and 1730 cm^{-1}; NMR δ 0.70 (s, 3, H_3C_{18}–), 0.90 (s, 3, 10β-H_3C–), 1.14 (s, 3, 4β-H_3C–), 3.75 (s, 3, H_3COOC–), and 4.02 ppm (m, 1, 3α-H).

Anal. Calcd for $C_{22}H_{36}O_3$: C, 75.81; H, 10.41. Found: C, 75.78; H, 10.48.

4β-Carbomethoxy-4α-methylandrostan-3β-ol (40). Reduction of 0.042 g (0.12 mmol) of **26** with $NaBH_4$ in exactly the same manner as **12** afforded 0.043 g of crude product which was purified in the same manner used in the preparation of **39** to afford 0.035 g (83%) of **40** and 0.007 g of polar material, presumably diol. Recrystallization from isopropyl alcohol afforded 0.020 g (48%) of **40**: mp 129–130°; ir 3600 and 1730 cm^{-1}; NMR δ 0.70 (s, 3, H_3C_{18}–), 0.74 (s, 3, 10β-H_3C–), 1.37 (s, 3, 4α-H_3C–), 2.95–3.25 (m, 1, 3α-H), and 3.72 ppm (s, 3, H_3COOC–).

Anal. Calcd for $C_{22}H_{36}O_3$: C, 75.81; H, 10.41. Found: C, 75.70; H, 10.44.

4α-Carbomethoxy-4β,10β-dimethyl-*trans*-decal-3β-ol (41). Reduction of 0.399 g (1.7 mmol) of **27** with $NaBH_4$ in exactly the same manner as **12** afforded 0.411 g of crude oily product which was purified by preparative TLC, using 2:1 hexane–ether twice, to afford 0.088 g (21%) of material tentatively identified as 4α-carbomethoxy-4β,10β-dimethyl-*trans*-decal-3α-ol, 0.29 g (72%) of **41**, and 0.020 (5%) of polar material, presumably diol. Compound **41** was sublimed thrice at 70° (15 mm) to yield 0.150 g (37%) of white needles: mp 87–88°; ir 3400 and 1740 cm^{-1}; NMR δ 0.95 (s, 3, 10β-H_3C–), 1.10 (s, 3, 4β-H_3C–), 3.66 (s, 3, H_3COOC–), and 4.00 ppm (br t, 1, 3α-H).

Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.06. Found: C, 70.05; H, 10.04.

4β-Carbomethoxy-4α,10β-dimethyl-*trans*-decal-3β-ol (42). Reduction of 0.200 g (0.9 mmol) of **28** with $NaBH_4$ in exactly the same manner as **12** afforded 0.264 g of crude product which was purified by preparative TLC, using 2:1 hexane–ether twice to afford 0.043 g of material tentatively identified as 4β-carbomethoxy-4α,10β-dimethyl-*trans*-decal-3α-ol, 0.212 g of crude **42**, and 0.008 g of polar material, presumably diol. Compound **42** was sublimed twice at 65° (15 mm) to yield 0.120 g (56%) of white needles: mp 70–71°; ir 3500 and 1730 cm^{-1}; NMR δ 0.75 (s, 3, 10β-H_3C–), 1.35 (s, 3, 4α-H_3C–), 2.95–3.25 (br m, 1, 3α-H), and 3.70 ppm (s, 3, H_3COOC–).

Anal. Calcd for $C_{14}H_{24}O_3$: C, 69.96; H, 10.06. Found: C, 70.16; H, 9.90.

4α-Hydroxymethyl-4β-methylcholestan-3β-ol (2). Diol **2** was prepared by treatment of both **37** and **21** with $LiAlH_4$. Reduction of 0.050 g (0.11 mmol) of **21** with $LiAlH_4$ was performed exactly as with **11** to afford 0.047 g of crude product, mp 195–216°. One recrystallization from ether gave 0.034 g (78%) of **2**, mp 215–217°. Further recrystallization from ether afforded an analytical sample as glistening plates: mp 219–220°; ir 3350 cm^{-1}; NMR δ 0.64 (s, H_3C_{18}–), 0.80 (s, 10β-H_3C–), and ~3.5 ppm (br m, 3α-H and 4β-HOH_2C–).

Anal. Calcd for $C_{29}H_{52}O_2$: C, 80.49; H, 12.11. Found: C, 80.54; H, 12.27.

4β-Hydroxymethyl-4α-methylcholestan-3β-ol (3). Diol **3** was prepared by treatment of both **38** and **22** with $LiAlH_4$. Reduction of 0.58 g (1.5 mmol) of **22** with $LiAlH_4$ was performed exactly as with **11** to afford 0.58 g of a crude product, mp 187–199°, which was purified by chromatography on 12 g of acid-washed alumina. Elution with ethyl acetate afforded 0.52 g (93%) of **3**, which tends to gel in many solvents, but can be recrystallized from ethyl acetate to afford an analytical sample: mp 209–210°; ir 3300–3200 cm^{-1}; NMR δ 0.63 (s, H_3C_{18}–), 0.82 (s, 10β-H_3C–), 1.18 (s, 4α-H_3C–), and ~3.8 ppm (br m, 3α-H and 4β-HOH_2C–).

Anal. Calcd for $C_{29}H_{52}O_2$: C, 80.49; H, 12.11. Found: C, 80.46; H, 12.02.

4α-Hydroxymethyl-4β-methylandrostan-3β-ol (4). Reduction of 0.020 g (0.05 mmol) of **39** with $LiAlH_4$ was performed exactly as with **12** to afford 0.020 g of crude product which was recrystallized from ether to give 0.010 g (63%) of pure **4** as white needles: mp 203–204°; ir ($CHCl_3$) 3400 cm^{-1}; NMR δ 0.69 (s, 3, H_3C_{18}–), 0.91 (s, 6, 4β-H_3C– and 10β-H_3C–), and 3.0–4.0 ppm (br m, 3α-H and 4α-HOH_2C–).

Anal. Calcd for $C_{21}H_{36}O_2$: C, 78.69; H, 11.32. Found: C, 78.54; H, 11.34.

4β-Hydroxymethyl-4α-methylandrostan-3β-ol (5). Reduction of 0.018 g (0.05 mmol) of **40** with $LiAlH_4$ was performed exactly as with **12** to afford 0.017 g of crude product which was recrys-

tallized from 20:1 ether–isopropyl alcohol to give 0.008 g (48%) of pure **5** as white prisms: mp 197–199°; ir 3400–3300 cm^{-1}; NMR δ 0.68 (s, 10β-H_3C– and H_3C_{18}–), 1.30 (s, 4α-H_3C–), and 3.25–4.10 ppm (complex m, 3α-H and 4β-HOH_2C–).

Anal. Calcd for $C_{21}H_{36}O_2$: C, 78.69; H, 11.32. Found: C, 78.71; H, 11.35.

4α-Hydroxymethyl-4β,10β-dimethyl-*trans*-decal-3β-ol (6). Reduction of 0.045 g (0.19 mmol) of **41** with $LiAlH_4$ was performed exactly as with **12** to afford 0.048 g of crude product which was sublimed at 80° (15 mm) to give 0.030 g (74%) of **6** as white plates: mp 97–98° (lit.[27] mp 107°); ir 3300 cm^{-1}; NMR δ 0.85 (s, 3, 10β-H_3C–), 0.95 (s, 3, 4β-H_3C–), and 2.75–3.70 ppm (complex m, 5).

Anal. Calcd for $C_{13}H_{24}O_2$: C, 73.53; H, 11.39. Found: C, 73.62; H, 11.42.

4β-Hydroxymethyl-4α,10β-dimethyl-*trans*-decal-3β-ol (7). Reduction of 0.042 g (0.18 mmol) of **42** with $LiAlH_4$ was performed exactly as with **12** to afford 0.032 g (86%) of crude **7**. Preparative TLC using 1:1 hexane–ether twice gave 0.015 g (40%) of pure **7** as a colorless oil: ir (neat) 3350 cm^{-1}; NMR δ 0.89 (s, 3, 10β-H_3C–), 1.19 (s, 3, 4α-H_3C–), and 3.1–4.25 ppm (br m, 5); M^+ *m/e* 212.1779 (calcd for $C_{13}H_{24}O_2$, 212.1776).

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Registry No.—**2,** 19418-66-7; **3,** 19418-67-8; **4,** 55161-93-8; **5,** 55161-94-9; **6,** 55161-95-0; **7,** 55220-84-3; **8,** 601-57-0; **9,** 2872-90-4; **10,** 4087-39-2; **11,** 38367-88-3; **12,** 55161-96-1; **13,** 55220-85-4; **14,** 3702-48-5; **15,** 19418-68-9; **15** diacetate, 55161-97-2; **16,** 55161-98-3; **16** diacetate, 55161-99-4; **17,** 55162-00-0; **18,** 55162-01-1; **19,** 55162-02-2; **20,** 55162-03-3; **21,** 55162-04-4; **22,** 22153-79-3; **23,** 22153-80-6; **24,** 22153-81-7; **25,** 55162-05-5; **26,** 55162-06-6; **27,** 55162-07-7; **28,** 55162-08-8; **31,** 984-86-1; **32,** 861-13-2; **33,** 5062-43-1; **34,** 55162-09-9; **35,** 3669-27-0; **36,** 55162-10-2; **37,** 55162-11-3; **38,** 55162-12-4; **39,** 55162-13-5; **40,** 55162-14-6; **41,** 55162-15-7; **42,** 55162-16-8; 4α-carbomethoxyandrostan-3α-ol, 55162-17-9; 4α-carbomethoxy-10β-methyl-*trans*-decal-3α-ol, 55162-18-0; methyl iodide, 74-88-4; 4α-methylandrostan-3α-ol, 55162-19-1.

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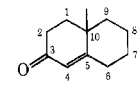

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