Chromatography of the residue on alumina, activity IV, and elution with benzene gave 40 mg of oily **12**: ir (CCl_4) NH 3.18 (m), C=O 6.00 (s), C=C 6.32 μ (s). In view of its instability, it was used for the next reaction without further purification.

A solution of 40 mg of **12** in 10 ml of 10% methanolic potassium hydroxide was stirred at room temperature under nitrogen for 30 hr. It was neutralized with 10% hydrochloric acid and evaporated. Extraction of the residue with ethanol and evaporation of the extract gave 10 mg of a viscous oil which crystallized slowly. Crystallization from ethyl acetate–ethanol yielded 4 mg of prisms of *dl*-18,19-dihydroantirhine (**5**): mp 95–97.5°; infrared, ultraviolet, mass spectral, and tlc characteristics identical with those of an authentic sample;[6,13] *m/e* 298.204516 (calcd 298.204503).

Methyl Demethylilludinate (14).—A solution of dry potassium *tert*-butoxide (from 620 mg of potassium) and 3.24 g of diester **7c** in 25 ml of 1,2-dimethoxyethane was added dropwise to 1.75 g of 3,3-dimethylcyclopentanone[15] over a 1-hr period and the mixture was stirred at room temperature under nitrogen for 15 hr. Hydrochloric acid (50 ml of 3 *N*) was added and the mixture was evaporated at 50° to dryness. The residue was dried further in a vacuum desiccator for 12 hr and then dissolved in 50 ml of methanol saturated with hydrogen chloride gas. After 2 hr, the mixture was worked up in a previously described manner[17] and the crude product was chromatographed on alumina (activity III) and eluted with a 3:2 mixture of cyclohexane–benzene. Crystallization of the product from pentane gave 2.98 g of colorless crystals, mp 38–45°, whose sublimation afforded the diesters **13** and its stereoisomer: mp 45–55°; ir (KBr) C=O 5.78 (s), 5.81 (s), C=C 6.12 (m), 6.31 (m), 6.48 (m); uv (MeOH) λ_{max} 224 nm (log ϵ 4.36); pmr ($CDCl_3$) δ 0.93 (s, 3, Me), 1.08 (s, 3, Me), 1.62 (t, 2, J = 8 Hz, CH_2 of major isomer), 1.88 (broad s, 2,allyl CH_2 of major isomer), 2.18 (t, 2, J = 8 Hz, CH_2 of minor isomer), 2.83 (broad s, 2, allyl CH_2 of minor isomer), 3.10 (t, 2, J = 8 Hz, allyl CH_2 of major isomer), 3.61 (s, 3, OMe), 3.82 (s, 3, OMe), 7.12 [t, 1, J = 4 Hz, C(5) H], 8.68 [d, 1, J = 4 Hz, C(6) H], 9.13 [broad s, 1, C(2) H].

Anal. Calcd for $C_{17}H_{21}O_4N$: C, 67.29; H, 6.98; N, 4.62. Found: C, 67.13; H, 7.08; N, 4.63.

A solution of 733 mg of diester **13** and its stereoisomer in 5 ml of dry 1,2-dimethoxyethane was added to a solution of potassium *tert*-butoxide (from 104 mg of potassium) in 25 ml of 1,2-dimethoxyethane and the intensely red solution was stirred under nitrogen for 0.5 hr. The color had disappeared and the mixture was evaporated to dryness. The residue was treated with 10 ml of water and the mixture was brought to pH 6 with 5% hydrochloric acid and extracted with methylene chloride. The extract was dried over anhydrous sodium sulfate and evaporated. Crystallization of the residue from ethyl acetate yielded 525 mg of yellow, crystalline ester **14**: mp 220° dec; ir (Nujol) C=O 5.87 (s), C=C 6.14 (s), 6.27 (w), 6.38 (s); uv (MeOH) λ_{max} 242 nm (log 4.63), 285 (4.03), 307 (4.01), 333 (3.98), 385 (3.66); $\lambda_{shoulder}$ 260 nm (log ϵ 4.33), 348 (3.93); pmr (DMSO-d_6) δ 2.85 (s, 2, CH_2), 3.08 (s, 2, CH_2), 3.92 (s, 3, OMe), 8.23 (d, 1, J = 6 Hz, pyridine β H), 8.45 (d, 1, J = 6 Hz, pyridine α H), 9.50 (s, 1, pyridine α' H).

Anal. Calcd for $C_{16}H_{17}O_3N$: C, 70.83; H, 6.32; N, 5.16. Found: C, 71.10; H, 6.47; N, 5.33.

Registry No.—**5**, 42289-79-2; **6**, 42253-62-3; **6** picrate, 42289-80-5; **7a**, 33402-75-4; **7b** enolate, 42253-64-5; **7c**, 33402-74-3; **8**, 33402-73-2; **9a**, 42253-67-8; **9b**, 42253-68-9; **10**, 42253-69-0; **11b**, 42253-70-3; **12**, 42253-71-4; **13**, 42253-72-5; **13** stereoisomer, 42253-73-6; **14**, 42253-74-7; dimethyl oxalate, 553-90-2.

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Steroids Derived from Bile Acids. A Novel Side-Chain Degradation Scheme

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A four-step degradative sequence of methyl cholanate (**1**) and methyl lithocholate (**13**) is described with a 35 and 27% overall yield, respectively. The method involves conversion of the esters to the rearranged phenyl ketones (**4** and **16**) which are in turn subjected to a Norrish type II photoelimination. Ozonolysis of the final products leads to physiologically important steroid compounds.

In a recent publication[1] we have described a novel method for the degradation of the carbon chain of organic acids and their derivatives. The key substance in the sequence we have described is a phenyl ketone which is easily obtainable by an established[2] rearrangement procedure. In view of the intensive recent interest[3-7] in the photolysis of such compounds by Norrish type II processes, we have decided to utilize this reaction, combine it with a part of our previous scheme, and apply it to the degradation of the side chain of steroidal substrates. Thus a convenient modification of the original degradative sequence has resulted, the individual steps of which are outlined in Scheme I.

Results and Discussion

Samples of esters **1** and **13** were converted to the corresponding tertiary alcohols **2** and **14** by means of a standard Grignard reaction with phenylmagnesium bromide in nearly quantitative yields. Dehydration of the alcohols in acetic anhydride afforded the corresponding olefins **3** and **15**. The yields for this step were 85%. The olefins **3** and **15** were easily and quantitatively converted to the corresponding ketones **4** and **16** by means of the Kakis reaction.[2] This reaction in the present system generates a pair of diastereomers, epimeric around the C_{23} asymmetric carbon. Although not directly related to the degradative scheme, which utilizes the mixture, we thought it would be of theoretical as well as practical interest to separate the stereoisomers and to obtain the spectra and their physical constants. This seemed to be particularly appropriate since these compounds have never been prepared before and their physiological properties are not known. Separation was achieved by laborious thin-layer chromatography. The pure isomers were isolated and their melting points, optical rotations, and nmr spectra were obtained.

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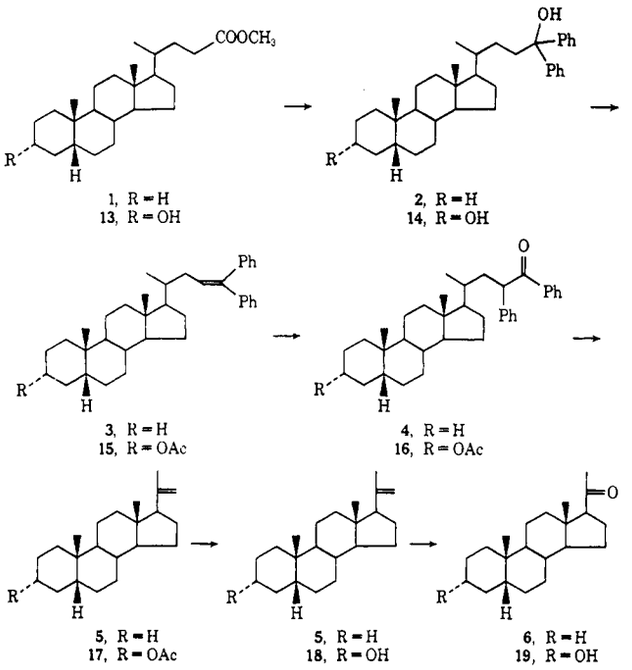
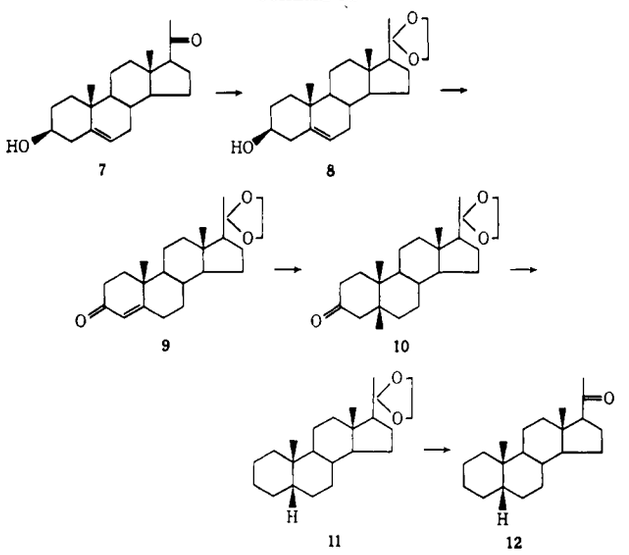
SCHEME I



SCHEME II



The mixtures of ketones **4** and **16** were subjected to the conditions of the Norrish type II photoelimination, which resulted in a complex mixture of products. Separation of the mixtures by thin-layer chromatography afforded the degradation products **5** and **17** in 45 and 35% yields, respectively. No attempt was made to isolate or identify the other photolysis products.

We have found by means of repeated trials that a small increase in the yields occurs when the photolysis is carried out in *tert*-butyl alcohol instead of benzene.

Identification of structure was obtained by infrared and nuclear magnetic resonance spectroscopy and by elemental analysis. To obtain final confirmation, samples of compounds **5** and **18** were subjected to standard ozonolysis and the corresponding ketones **6** and **19** were compared and found to be identical with authentic samples. An authentic sample of compound **19** was obtained commercially.[8] The other authentic sample, compound **6**, was synthesized from pregnenolone (**7**) *via* a five-step synthesis, the details of which are shown in Scheme II.

The degradative scheme (I) described above afforded a 35 and 27% overall yield for the four-step degradation of methyl cholanate and methyl lithocholate, respectively. These yields are significantly higher than those obtained by many other published pathways.[9-14] We are currently investigating its application to the degradation of the lanosterol side chain and other steroidal substrates. Finally, it is noteworthy that the terminal products of our pathway are useful precursors of physiologically important compounds.[15]

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Experimental Section

General.—Melting points were taken on a Kofler apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 257 spectrophotometer. Nmr spectra were determined on a Joel Model C60H spectrometer using tetramethylsilane as internal standard and are reported in parts per million. Optical rotations were measured with the aid of a Perkin-Elmer Model 141 polarimeter. Irradiations were performed with a Hanau TQ 150-W medium-pressure mercury lamp contained in a quartz immersion well. The 3130-Å line was isolated with a 1-cm path of 0.002 *M* potassium chromate in a 5% aqueous solution of potassium carbonate. The required cooling was achieved by circulation of this solution. Microanalysis were performed by the microanalysis service of CNRS at the Gif Sur Yvette Laboratories in France.

24,24-Diphenyl-24-hydroxy-5β-cholane (2).—This compound was prepared from a sample (17 g, 0.0227 mol) of pure (mp 87–88°) methyl cholanate (**1**) by the standard addition of phenylmagnesium bromide (57.8 g, 0.227 mol) in anhydrous ether. After hydrolysis of the reaction mixture and decomposition with a saturated solution of ammonium chloride, a viscous yellow oil (27 g) was obtained. After purification by column chromatography over silica (Merck 0.05–0.2 mm) using a pentane–ether mixture as the eluent (10:1), 21.9 g of alcohol **2** were obtained. The crystallization from hexane (−10°) afforded a pure (mp 95–96°) product in 96% yield: ir (CCl_2CCl_2) 3610, 3080, 3060, 3030, and 700 cm^{-1}; nmr ($CDCl_3$) 0.62, 0.89 (3 H, singlet, C_{18} and C_{19} protons), 7.1–7.6 (10 H, multiplet, aromatic protons).

Anal. Calcd for $C_{36}H_{50}O$: C, 86.69; H, 10.11; O, 3.21. Found: C, 86.47; H, 9.97; O, 3.28.

24,24-Diphenyl-5β-chol-23-ene (3).—This compound was prepared by dehydrating a sample of alcohol **2** (8.8 g) in refluxing acetic anhydride for a period of 12 hr. After removal of the solvents by rotatory evaporation and one recrystallization from methanol–ether, a crystalline sample (8.2 g) was obtained. Further purification was achieved by column chromatography over silica (Merck, 0.05–0.2 mm) using pentane as the eluent. Thus a pure (mp 120–122°) sample (7.1 g, 84%) of olefin **3** was obtained: ir (CCl_2CCl_2) 3080, 3060, 3020, 1600, and 700 cm^{-1}; nmr ($CDCl_3$) δ 0.61, 0.9 (singlet, C_{18} and C_{19} protons), 6.1 (1 H, triplet, ethylenic, J = 7.5 Hz), 7–7.6 (10 H, multiplet, aromatic protons).

Anal. Calcd for $C_{36}H_{48}$: C, 89.94; H, 10.06. Found: C, 89.77; H, 10.03.

23,24-Diphenyl-5β-cholan-24-one (4).—A sample (1.3 g) of olefin **3** was converted to ketone **4** by the Kakis method.[2] The reaction afforded 1.27 g (94%) of sufficiently pure ketone **4**: ir (CCl_2CCl_2) 3090, 3060, 3030, 1690, 1600, 1450, and 700 cm^{-1}.

Anal. Calcd for $C_{36}H_{48}O$: C, 87.04; H, 9.74; O, 3.22. Found: C, 86.74; H, 9.45; O, 3.24.

This reaction results in a mixture of two (**4a** and **4b**) diastereomers, epimeric around the C_{23} asymmetric carbon. The stereoisomers were separated by thin-layer chromatography on fluores-

cent silica using several successive elutions with pentane–ether (50:1). Subsequently, each isomer was recrystallized from methanol. The least polar substance (**4a**) melted sharply at 146–146.5°. The other isomer (**4b**) melted sharply at 158–159°: nmr (**4a**) ($CDCl_3$) δ 0.6, 0.9 (singlets, C_{18} and C_{19} protons), 4.77 (multiplet, 1 H, proton α to the carbonyl), 7.05–8.2 (10 H, multiplet, aromatic protons); nmr (**4b**) 0.47, 0.87 (singlets, C_{18} and C_{19} protons), 4.65 (multiplet, 1 H, proton α to the carbonyl), 7.1–8.2 (10 H, multiplet, aromatic protons); $[\alpha]D$ ($CHCl_3$) (**4a**) −73°, $[\alpha]D$ ($CHCl_3$) (**4b**) +96.5°.

20-Methylene-5β-pregnane (5).—A sample (1 g) of the diastereomeric mixture of ketones (**4**) was dissolved in anhydrous *tert*-butyl alcohol (70 ml) and irradiated for a period of 3 hr. On evaporation of the solvents under vacuum, a sample (1.03 g) of crude (yellow oil) product was obtained. Purification was achieved by thin-layer chromatography on silica containing 8% silver nitrate. After three elutions with pentane–ether (40:1) a pure sample (275 mg; *ca.* 45%; R_f 0.7) of olefin **5** was obtained which crystallized spontaneously. Recrystallization was achieved with some difficulty from methanol–ether producing the analytical sample (mp 72–74°): ir (CS_2) 3080 and 885 cm^{-1}; nmr ($CDCl_3$) δ 0.57, 0.95, 1.77 (singlets, C_{18}, C_{19}, and C_{21} protons), 4.7, 4.85 (2 H, two adjacent singlets, exocyclic methylene protons); $[\alpha]D$ ($CHCl_3$) +12.5°.

Anal. Calcd for $C_{22}H_{36}$: C, 87.92; H, 12.08. Found: C, 87.53; H, 12.02.

The above irradiation was repeated many times. The yields in *tert*-butyl alcohol ranged from 45 to 48% and in benzene from 35 to 40%.

Pregnenolone Ethylene Ketal (8).—A commercial sample (29 g, 0.091 mol) of pregnenolone (**7**) was converted to the ethylene ketal (**8**) by a standard method.[16] Thus 31 g (95%) of crude product was obtained. After recrystallization from methanol containing a few drops of pyridine a pure sample of ketal **8** was obtained which melted at 164–166° in agreement with the literature:[16] ir (CS_2) 3610, 1070, 1050, 1025, and 950 cm^{-1}; nmr ($CDCl_3$) δ 0.81 (3 H, singlet, C_{18} protons), 1.05 (3 H, singlet, C_{19} protons), 1.33 (3 H, singlet, C_{21} protons), 3.5 (1 H, C_3 proton), 3.93 (4 H, multiplet, $-OCH_2CH_2O-$), 5.37 (1 H, multiplet, ethylenic proton).

Progesterone 20-Ethylene Ketal (9).—A sample of pregnenolone ethylene ketal (**8**) above (15.6 g, 0.044 mol) was converted by a standard Oppenauer oxidation to progesterone ethylene ketal (**9**). The yield of the crude product (13.9 g) was 89%. Recrystallization from methanol containing a few drops of pyridine afforded a pure product (mp 189–191°) whose melting point was in agreement with the literature value:[16] ir (CS_2) 1680, 1070, 1050, and 950 cm^{-1}; nmr ($CDCl_3$) δ 0.71 (3 H, singlet, C_{18} protons), 1.2 (3 H, singlet, C_{19} protons), 1.3 (3 H, singlet, C_{21} protons), 3.9 (4 H, multiplet, $-CH_2CH_2O-$), 5.7 (1 H, singlet, C_4 proton).

20-Ethylenedioxy-5β-pregnane-3-one (10).—This compound was prepared by an adaptation of a previously reported method.[17] Thus a sample of progesterone ethylene ketal (**9**) (5 g, *ca.* 0.014 mol) in freshly distilled *N*-methylpyrrolidine (250 ml) was treated with a commercial sample[18] (2.5 g, 5% Pd on $CaCO_3$) of the catalyst and hydrogenated. At the end of the reaction a white crystalline product (5.1 g) was isolated which consisted of a mixture of the two stereoisomers with the 5β isomer predominating. On recrystallization from acetone containing a few drops of pyridine a pure sample (2.7 g, mp 172–174°) of the 5β isomer was obtained. Column chromatography of the mother liquors over silica (Merck 0.05–0.2 mm) with pentane–ether (1:1) afforded an additional sample (1.55 g) of the pure 5β isomer (total yield ~80%): ir (CS_2) 1715, 1070, 1050, and 950 cm^{-1}; nmr ($CDCl_3$) δ 0.77 (3 H, singlet, C_{19} protons), 0.9 (3 H, singlet, C_{18} protons), 1.32 (3 H, singlet, C_{21} protons), 3.57 (4 H, multiplet, $-OCH_2CH_2O-$). Final confirmation of the structure of **10** was obtained by hydrolysis of a small sample which afforded 5β-pregnane-3,20-dione whose melting point (123–124°) and spectra were in agreement with previously reported values.[19]

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20-Ethylenedioxy-5β-pregnane (11).—This compound was prepared by a standard Wolff–Kishner reduction of a sample (2.8 g, *ca.* 0.008 mol) of compound **10**. Thus a white crystalline product (2.6 g, 95%) was obtained, and recrystallized from acetone containing a few drops of pyridine. The pure sample melted at 110–112°: ir (CS_2) 1070, 1050, and 950 cm^{-1}; nmr ($CDCl_3$) δ 0.72 (3 H, singlet, C_{19} protons), 0.9 (3 H, singlet, C_{18} protons), 2.3 (broad band, methylenes, and C_{21} methyl protons), 3.9 (4 H, multiplet, $-OCH_2CH_2O-$).

5β-Pregnan-20-one (12). A.—A sample of ethylene ketal **11** (2.6 g) was hydrolyzed in acetic acid–water (1:1, 100 ml) for a period of 3 hr. To increase the solubility it was necessary to add some methylene chloride. At the end of the reaction the mixture was neutralized with concentrated ammonium hydroxide, diluted with water, and extracted with methylene chloride. On drying the extracts and evaporation of the solvent, a crude crystalline product (2.5 g) was obtained. After recrystallization in ethanol a pure sample (mp 114–116°) of ketone **12** was obtained: ir (CS_2) 1705 cm^{-1}; nmr ($CDCl_3$) δ 0.6 (3 H, singlet, C_{18} protons), 0.92 (3 H, singlet, C_{19} protons), 2.1 (3 H, singlet, C_{21} protons). The above physical constants were in complete agreement with previously reported values.[15]

B.—To obtain final confirmation of compound **5** a small sample was subjected to ozonolysis in the usual way. This afforded a keto steroid whose melting point and ir and nmr spectra were identical with those of the authentic sample of 5β-pregnan-20-one (**12**) independently prepared above. When mixture melting points were taken there was no temperature depression.

3α,24-Dihydroxy-24,24-diphenyl-5β-cholane (14).—This compound was prepared by a standard Grignard reaction in tetrahydrofuran. The procedure was identical with that reported above for compound **2**. Thus starting with a sample (25 g) of methyl lithocholate (**13**) we have obtained 31.15 g (95%) of pure (mp 146–147°) diol **14**: ir (CS_2) 3610, 3090, 3060, 3040, and 700 cm^{-1}; nmr ($CDCl_3$) δ 0.6, 0.9 (singlets, C_{18} and C_{19} protons), 3.52 (1 H, multiplet, 3β H), 7.1–7.6 (10 H, multiplet, olefinic protons).

3α-Acetoxy-24,24-diphenyl-5β-chol-23-ene (15).—Simultaneous acetylation of the 3-hydroxy and dehydration of the Grignard product **14** was achieved by refluxing a sample (24 g) of diol **14** with acetic anhydride–acetic acid (145 ml, 5:1) for a period of 5 hr. Upon the usual work-up and recrystallization from methanol–methylene chloride a pure sample (mp 161–163°, 85%) of compound **15** was obtained. The observed melting point was in agreement with that reported in the literature:[20] ir (CS_2) 3080, 3060, 3020, 1740, 1240 and 700 cm^{-1}; nmr ($CDCl_3$) δ 0.62, 0.93 (singlets, C_{18} and C_{19} protons), 2.0 (singlet, acetoxy protons), 4.72 (1 H, multiplet, 3β proton), 6.1 (1 H, triplet, ethylenic proton, J = 7.5 Hz), 7–7.5 (10 H, multiplet, aromatic protons).

3α-Acetoxy-23,24-diphenyl-5β-cholan-24-one (16).—This product was obtained from a sample of olefin **15** (5 g) by means of the Kakis method.[2] The reaction afforded 4.9 g (95%) of sufficiently pure ketone **16**: ir (CS_2) 3080, 3060, 3030, 1735, 1685, 1240, and 700 cm^{-1}.

Anal. Calcd for $C_{38}H_{50}O_3$: C, 82.26; H, 9.08; O, 8.65. Found: C, 82.41; H, 9.19; O, 8.69.

This reaction results in a mixture of two (**16a** and **16b**) diastereoisomers, epimeric around the C_{23} asymmetric carbon. Separation of these isomers proved to be difficult; nevertheless, we were able to obtain a pure sample of each by thin layer chromatography on fluorescent silica involving at least 12 successive elutions with pentane–ether (10:1). Subsequently, each isomer was recrystallized from methanol–ether. The least polar substance (**16a**) melted at 145–147° and the other (**16b**) at 146–148°. Owing to the closeness of the melting points, nmr spectra and optical rotations of the two isomers were also taken: nmr (**16a**) ($CDCl_3$) δ 0.65, 0.95 (singlets, C_{18} and C_{19} protons), 2.05 (singlet, acetoxy protons), 4.8 (multiplet, 2 H, proton α to carbonyl and 3β proton), 7.1–8.2 (10 H, multiplet, aromatic protons); nmr (**16b**) 0.5, 0.9 (singlet, C_{18} and C_{19} protons), 2.0 (singlet, acetoxy protons), 4.7 (2 H, multiplet, proton α to carbonyl and 3β proton), 7.1–8.2 (10 H, multiplet, aromatic proton); $[\alpha]D$ ($CHCl_3$) (**16a**), −33.5°; $[\alpha]D$ ($CHCl_3$) (**16b**), +76°.

3α-Acetoxy-20-methylene-5β-pregnane (17).—This compound was obtained by irradiation of a sample (1.8 g) of the ketone mixture **16**. A procedure identical with that described for the photolysis of compound **5** was followed, except that in the chromatography of the products a 10:1 pentane–ether mixture was used. Thus 450 mg (38%) of pure product were obtained which

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crystallized spontaneously. Recrystallization from methanol–ether at −10° afforded an analytical sample (mp 85–86.5°): ir (CS_2) 3080, 1740, 1240, and 885 cm^{-1}; nmr ($CDCl_3$) δ 0.55, 0.95, and 1.77 (singlets, C_{18}, C_{19}, and C_{21} protons), 2.05 (singlet, acetoxy protons), 4.62 and 4.75 (two adjacent singlets, exocyclic methylene and 3β protons); $[\alpha]_D$ ($CHCl_3$) +41°.

Anal. Calcd for $C_{24}H_{38}O_2$: C, 80.39; H, 10.68; O, 8.92. Found: C, 80.56; H, 10.52; O, 8.75.

The above irradiation was repeated many times. The yields in *tert*-butyl alcohol ranged from 35 to 38% and in benzene from 33 to 35%.

Final confirmation was obtained by lithium aluminum hydride reduction of the acetoxy compound **17** followed by standard ozonolysis of the resulting alcohol **18**. Thus a sample of 3α-hydroxy-5β-pregnan-20-one (**19**) was obtained whose physical constants and spectra were identical with those of an authentic sample.[8]

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Registry No.—**1**, 2204-14-0; **2**, 42151-39-3; **3**, 42151-40-6; **4a**, 42151-41-7; **4b**, 42151-42-8; **5**, 42151-43-9; **7**, 145-13-1; **8**, 2415-36-3; **9**, 978-98-3; **10**, 18000-86-7; **11**, 42151-47-3; **12**, 4729-67-3; **13**, 1249-75-8; **14**, 42151-48-4; **15**, 4144-29-0; **16a**, 42151-50-8; **16b**, 42151-51-9; **17**, 42151-52-0.

Synthesis of 4-Amino-4,6-dideoxy-D-allose Derivatives[1,2]

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Base-catalyzed isomerization of methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-*lyxo*-hexopyranosid-4-ulose (**2**) gave methyl 6-deoxy-2,3-*O*-isopropylidene-β-D-*ribo*-hexopyranosid-4-ulose (**3**) by inversion at C-5. Conversion of **3** to its oxime **6** followed by reduction with lithium aluminum hydride yielded methyl 4-amino-4,6-dideoxy-2,3-*O*-isopropylidene-β-D-allopyranoside (**7**). Acetylation of **7** with acetic anhydride in pyridine followed by hydrolysis of the isopropylidene group gave methyl 4-acetamido-4,6-dideoxy-β-D-allopyranoside (**8**), which was then deacetylated to give methyl 4-amino-4,6-dideoxy-β-D-allopyranoside (**9**). Conversion of **7** to several derivatives including the free sugar, 4-*N*,*N*-dimethylamino-4,6-dideoxy-D-allose (**12**), is discussed. Also, synthesis of methyl 6-deoxy-2,3-*O*-isopropylidene-α-D-*ribo*-hexopyranosid-4-ulose (**18**) and its conversion into methyl 4-amino-4,6-dideoxy-α-D-allopyranoside (**32**) and the *N*-acetate **33** are reported. Compound **33** was also obtained from 4-acetamido-4,6-dideoxy-2,3-di-*O*-methanesulfonyl-α-D-glucopyranoside (**35**) by internal displacement of the sulfonate ester at C-3 by the neighboring *N*-acetate followed by desulfonylation with sodium naphthalene reagent. The D-erythro stereochemistry at C-4 and C-5 of both **8** and **33** was confirmed by their degradation to D-allothreoninol.

The occurrence of several 4-amino-4,6-dideoxy sugar derivatives in biologically important natural sources[4] prompted us to undertake a comprehensive investigation on the synthesis and chemistry of this new class of carbohydrates. So far, the syntheses of the derivatives of seven of a possible total of eight of these hexoses (D series) have been recorded.[1,5] We now report the isomerization of an L-hexos-4-ulose into a D-keto sugar by base-catalyzed inversion at C-5 and the conversion of the new ketone into 4-amino-4,6-dideoxy-D-allose derivatives. A derivative of this amino sugar was also obtained from a 4-amino-4,6-dideoxy-D-glucose derivative by the internal displacement of a sulfonate ester at C-3 by the neighboring *N*-acetyl group.

Methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-*lyxo*-hexopyranosid-4-ulose[6,7] (**2**) was prepared from methyl 6-deoxy-2,3-*O*-isopropylidene-α-L-mannopyranoside[8] (**1**) by oxidation with either a mixture of dimethyl sulfoxide and phosphorus pentoxide in pyridine[1a] or with a catalytic amount of ruthenium tetroxide in the presence of sodium hypochlorite.[9,10] When a solution of **2** in 80% aqueous pyridine was heated at 100°, a small proportion of a new product was formed as shown by

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