incompatible with the sensitive β-hydroxy ester functionality present in atropine. Demethylation with trichloroethyl chloroformate[14] seemed potentially more useful, since trichloroethyl carbamates can be cleaved under mild conditions with Zn in AcOH.

In a trial experiment, treatment of atropine with Cl_3CCH_2OCOCl under conditions similar to those employed for the PhOCOCl demethylation of morphine[15] resulted in the quantitative formation of two nonbasic, oily compounds (ratio ~9:1), which were separated by column chromatography and assigned structures **8** and **9** on the basis of NMR and IR spectroscopy. When treated with Zn dust in AcOH, both **8** and **9** were converted into the same polar product, presumed to be noratropine.

On a preparative scale, the reaction mixture consisting of **8** and **9** was directly treated with Zn dust in AcOH to produce crystalline noratropine (**1**) in 90.5% yield. Care had to be exercised during the workup, since concentration of the filtered AcOH solution containing noratropine on a rotary evaporator at 60 °C gave primarily the dehydration product **10** (oxalate mp 268–269 °C, NMR (Me_2SO-d_6) δ 6.32 [d, J = 28 Hz]), again demonstrating the sensitivity of this system. Therefore, the basification–extraction scheme described below was adopted.

Experimental Section

A mixture of 5.0 g (17.3 mmol) of atropine (**7**), 12 mL (87 mmol) of Cl_3CCH_2OCOCl, 17.28 g (173 mmol) of $KHCO_3$, and 250 mL of $CHCl_3$ was refluxed for 4 h. The cooled mixture was filtered, the solvent removed on a rotary evaporator, and the residue freed from excess Cl_3CCH_2OCOCl (kugelrohr setup, oil pump, 80 °C). The remaining mixture of carbamates was stirred with 10 g of activated Zn dust[16] in 100 mL of AcOH at 15 °C for 16 h. Inorganic matter was filtered off and the filter cake was washed with AcOH (50 mL). The filtrate was diluted with 150 mL of H_2O and cooled in an ice bath. Aqueous NH_3 (58%) was added dropwise (T < 10 °C) with stirring to pH ~6, at which point the mixture was extracted with ether to remove a small amount of neutral material. Addition of NH_3 to the aqueous phase was continued to pH ~10. Extraction with four 150-mL portions of $CHCl_3$, washing the combined extracts with brine, drying over anhydrous K_2CO_3, and evaporating afforded 4.3 g (90.5%) noratropine (**1**) as colorless crystals, mp 114 °C (lit. mp 114 °C),[11] homogeneous on TLC (silica gel, 50 CH_2Cl_2/50 MeOH/1 Et_3N).

Acknowledgment. The author would like to thank Dr. John G. Moffatt for helpful discussions.

Registry No.—**1**, 16839-98-8; **7**, 51-55-8; **8**, 67393-86-6; **9**, 67393-87-7; Cl_3CH_2OCOCl, 17341-93-4.

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Side-Chain Extension of 17-Keto Steroids to 17α,22-Aldehydes

D. John Aberhart*[1] and Chi-Tung Hsu

Department of Chemistry, The Catholic University of America, Washington, D.C. 20064, and The Worcester Foundation for Experimental Biology, Shrewsbury, Massachusetts 01545

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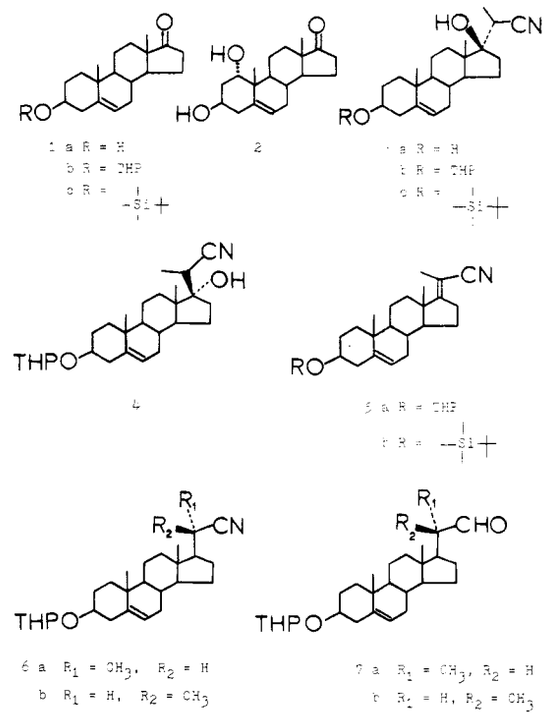
We wished to develop a method for side-chain extension of 17-keto steroids which could be applied to 1α,3β-dihydroxyandrost-5-en-17-one, readily available from 3β-hydroxyandrost-5-en-17-one by microbiological methods.[2] Thus an alternative route to the steroidal precursors of the clinically important 1α,25-dihydroxyvitamin D_3[3,4] and its analogues might become available. We now report a simple method of converting such 17-keto steroids into the 17α*H*-23,24-bisnorchol-5-en-22-al derivatives and related compounds.

3β-Hydroxyandrost-5-en-17-one (**1a**) was converted to the THP ether **1b**,[5] which upon treatment with excess propionitrile and lithium diisopropylamide (LDA)[6] at −78 °C for 90 min, followed by addition of the cold solution to water, gave a single product **3b** (88%). The 17β orientation of the hydroxyl in **3b** is assigned from mechanistic considerations and from the observed downfield shift of the C-18 methyl NMR signal (δ 0.88 in **1b**) to δ 0.95. The product was formed as a mixture of epimers at C-20, which was not resolvable by recrystallization or thin-layer chromatography. In the presence of $Eu(fod)_3$ (ca. 1 equiv), the originally sharp C-18 methyl singlet became shifted substantially downfield, and appeared as two singlets of nearly equal intensity at δ 1.18 and 1.21.[7]

When the propionitrile addition reaction was conducted by stirring the reactants at −78 °C for 20 min followed by stirring at 25 °C for 20 h before workup, a mixture of **3b** and an isomeric product assigned the structure **4** (ratio of **3b**–**4**, ca. 1:2) was obtained in very low yield, accompanied by recovered starting material (80%). After recrystallization of the **3b** + **4** mixture, the pure **4** was obtained. Product **4** closely



resembled **3b** in its IR and ^1H NMR spectra. The latter were practically superimposable in the region δ 3.0–6.0, and differed mainly in the chemical shifts of the C-20–H (**3b**, δ 2.74; **4**, δ 2.85), C-21 methyl (**3b**, 1.47; **4**, δ 1.42), and C-18 methyl (**3b**,

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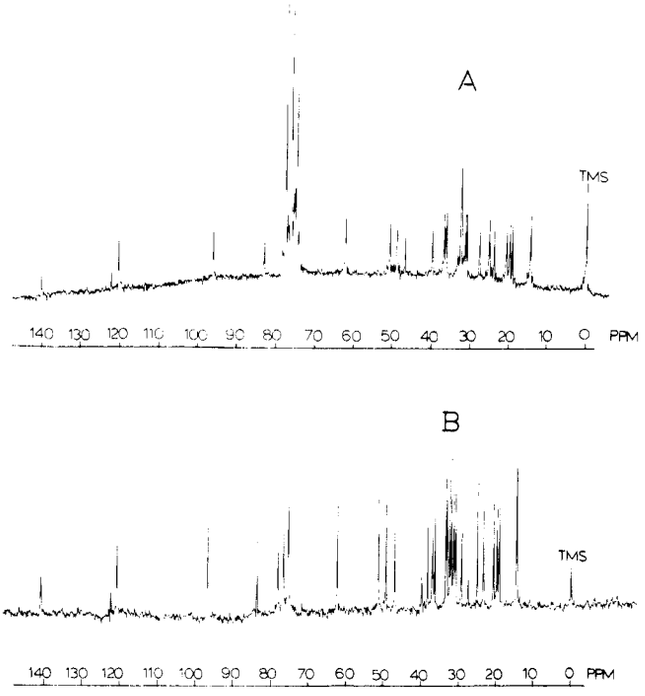

Figure 1: ^{13}C NMR spectra: A, compound **4**, 0.03 M in $CDCl_3$; B, compound **3b**, 0.16M in $CDCl_3$.

δ 0.95; **4**, δ 0.90). Furthermore the ^{13}C NMR (Figure 1) were nearly superimposable in all regions of the spectra except for slight differences in the δ 20–40 region. In the presence of $Eu(fod)_3$, again the ^1H signal for the C-18 methyl group was shifted downfield, appearing as two singlets at δ 1.25 and 1.28[8] of approximately equal intensities. Since both products **3b** and **4** were thereby demonstrated to consist of an epimeric mixture (presumably at C-20), it follows that if **3b** is to be formulated as the 17β-OH isomer, then **4** must be the 17α-OH isomer. The higher field C-18 methyl signal of **4** supports its formulation as the 17α-OH isomer. Both **3b** and **4** on treatment with lithium diisopropylamide (without propionitrile) at −78 °C slowly underwent fragmentation to their precursor, **1b**. Thus, it appears that addition of propionitrile anion to the 17-keto group is reversible. Under the low-temperature conditions, the kinetically controlled product **3b** is formed exclusively, whereas at higher temperature, a moderate amount of the more stable **4** is generated. However, at this temperature, reversion to starting material becomes predominant, and a very low yield of the addition products is obtained.

Following the method used for the production of **3b**, the *tert*-butyl dimethylsilyl ether **1c** and the unprotected **1a** gave with propionitrile and LDA (−78 °C, 90 min) in good yields the addition products **3c** and **3a**, respectively. Upon treatment with thionyl chloride in benzene–pyridine, **3b** and **3c** underwent nearly quantitative dehydration to **5a** and **5b**, respectively. The products were, presumably, $E + Z$ mixtures as indicated by the broadened vinyl methyl signal (δ 1.83), although both were chromatographically homogeneous and had sharp melting points. We did not separate the $E + Z$ mixtures of **5a** or **5b**. The sequence **1b** or **1c** → **5a** or **5b** provides a simple, high-yield alternative to the Wittig reaction approach recently reported by Watt et al.[9] for the interconversion of **1b** to **5a**, which in turn can be converted into progesterone.[9] Attempted selective dehydration of **3a** gave unsatisfactory results.

Reduction of **5a** to the 17αH saturated nitrile **6** was carried out with magnesium in methanol, essentially as previously described,[9] except that the THP ether was not hydrolyzed before workup. The product consisted of an inseparable 2:1 mixture of the 20*S* isomer **6a** (major) and 20*R* isomer **6b** as shown by the relative intensities of doublets in the NMR spectrum at δ 1.33 (major) and δ 1.29 (minor). The structural assignment is based on the conversion of the mixture into a corresponding mixture of aldehydes **7** which can be identified. Attempts to carry out a similar reduction of the *tert*-butyl dimethylsilyl ether **5b** were foiled by its extreme insolubility in methanol.

Further treatment of **6** with diisobutylaluminum hydride[10] gave a mixture of aldehydes **7a** and **7b** (87%) in a ca. 2:1 ratio, as shown by the signals for the C-18 methyl group at δ 0.68 (**7b**, minor) and δ 0.72 (**7a**).[11] After recrystallization of the mixture, the pure isomer **7a** was isolated, albeit in rather low yield (20%). Thus the sequence **1a** → **7** provides a partially satisfactory solution to the problem of side-chain assembly[12] and should be applicable to other 17-keto steroids such as **2**.[13]

Experimental Section

Melting points were taken on a hot-stage apparatus and are corrected. Specific rotations were measured on a Rudolph Model 80 polarimeter. Tetrahydrofuran (THF) was dried by distillation from $LiAlH_4$. Benzene was dried by shaking with concentrated H_2SO_4, followed by distillation. Diisopropylamine and pyridine were dried by distillation from barium oxide. Silica gel HF 254 + 366 (E. Merck) was used for thin-layer chromatography (TLC) in the solvents noted. IR spectra were determined in $CHCl_3$ solution on a Perkin-Elmer Model 237 or 337 spectrometer. ^1H NMR spectra were obtained in $CDCl_3$ solutions on Varian A-60, EM-360, or HA-100 instruments, with tetramethylsilane as internal reference. ^{13}C NMR spectra were obtained in $CDCl_3$ solutions on a Bruker SXP 22/100 spectrometer operating at 22.63 MHz. Peak positions are expressed in ppm (δ) downfield from Me_4Si. Mass spectra were determined on a Nuclide 12-90-G mass spectrometer equipped with a Nuclide DA/CSI.2 data acquisition system. Microanalyses were performed by Chemalytics, Inc., Tempe, Ariz.

3β-*tert*-Butyldimethylsilyloxyandrost-5-en-17-one (1c). 3β-Hydroxyandrost-5-en-17-one (1 g, 3.47 mmol) was stirred with *tert*-butyldimethylchlorosilane (630 mg, 4.2 mmol) and imidazole (585 mg, 8.6 mmol) in DMF (8 mL) at room temperature for 19 h. Then water (50 mL) and ether (50 mL) were added, and the ether extract was washed with dilute HCl, water, and saturated NaCl, dried (Na_2SO_4), and evaporated. Crystallization from methanol gave **1c**: 1.0 g, blades; mp 145–147 °C; IR ν 2950, 1740 cm^{-1}; NMR δ 0.05 (s, 6), 0.90 (12 H, s), 1.04 (s, 3, 19-CH_3), 3.50 (br m, 1, $W_{1/2}$ = 20 Hz, 3α H), 5.37 (br d, 1, J = 5 Hz, vinyl H).

Anal. Calcd for $C_{25}H_{42}O_2Si$: C, 74.55; H, 10.52. Found: C, 74.67; H, 10.60.

22-Cyano-17β-hydroxy-3β-tetrahydropyran-2′-yloxy-17α-pregn-5-ene (3b). To a solution of dry diisopropylamine (6 g, 59.4 mmol) in dry THF (150 mL) at −78 °C under N_2 was added a solution of *n*-butyllithium in hexane (59.4 mL, 1.0 M) followed immediately by propionitrile (3.0 g, 54.5 mmol) in dry THF (10 mL). The mixture was stirred 10 min at −78 °C, then **1b** (7.5 g, 20.2 mmol) in dry THF (12 mL) was added dropwise over 5 min. Stirring was continued for 90 min. The cold mixture was diluted with ether and water, and the ether solution washed with dilute HCl, 10% $NaHCO_3$, water, and saturated NaCl, dried (Na_2SO_4), and evaporated. The product was crystallized from ethanol–ether, giving 7.5 g of **3b**: needles; mp 175–177 °C; $[\alpha]^{23}D$ −77° (*c* 1.6, $CHCl_3$); IR ν 3850, 2240 cm^{-1}; NMR δ 0.95 (s, 3, 18-CH_3), 1.03 (s, 3, 19-CH_3), 1.47 (d, 3, J = 7 Hz, 21-CH_3), 2.74 (q, 1, J = 7 Hz, 20-H), 3.5 (m, 2), 3.85 (m, 1), 4.73 (br s, 1, $W_{1/2}$ = 6 Hz, 2′-H), 5.34 (br d, 1, J = 4 Hz, vinyl H).

Anal. Calcd for $C_{27}H_{41}NO_3$: C, 75.84; H, 9.66; N, 3.28. Found: C, 76.16; H, 9.84; N, 3.39.

In a similar manner, **1c** (2.0 g, 5 mmole) was converted to **3β-*tert*-butyldimethylsilyloxy-22-cyano-17β-hydroxy-17α-pregn-5-ene (3c)** (1.94 g, 85%): blades from ethanol–ether; mp 210–212 °C; IR ν 3580, 2235 cm^{-1}; NMR δ 0.06 (s, 6), 0.90 (s, 9), 0.97 (s, 3, 18-CH_3), 1.02 (s, 3, 19-CH_3), 1.48 (d, 3, J = 7 Hz, 21-CH_3), 2.77 (q, 1, J = 7 Hz, 20-H), 3.5 (br s, 1, $W_{1/2}$ = 20 Hz, 3α-H), 5.34 (br d, 1, J = 5 Hz).

Anal. Calcd for $C_{28}H_{47}NO_2Si$: C, 73.45; H, 10.36; N, 3.06. Found: C, 73.76; H, 10.34; N, 2.91.

Similarly, **1a** (1.0 g, 3.47 mmol) was converted to **22-cyano-3β,17β-dihydroxy-17α-pregn-5-ene (3a)** (0.98 g, 84%): prisms from $CHCl_3$; mp 214–217 °C; IR ν 3600, 2225 cm^{-1}; NMR δ 0.94 (s, 3, 18-CH_3), 1.03 (s, 3, 19-CH_3), 1.44 (d, 3, J = 7 Hz, 21-CH_3), 3.77 (q, 1, J = 7 Hz, 20-H), 3.55 (br s, 1, $W_{1/2}$ = 20 Hz, 3α-H), 5.38 (br s, 1, $W_{1/2}$ = 10 Hz, vinyl H); mass spectrum, m/e 343 (M^+, 58, $C_{22}H_{33}NO_2$ requires 343), 325 (61), 310 (39), 270 (26), 246 (44), 228 (54), 213 (100), 145 (70), 107 (54).

22-Cyano-17α-hydroxy-3β-tetrahydropyran-2′-yloxypregn-5-ene (4). To a solution of diisopropylamine (315 mg, 3.1 mmole) in dry THF (15 mL) containing triphenylmethane (10 mg) at −78 °C under N_2 was added n-butyllithium in hexane (3.1 mL, 1 M) followed by propionitrile (170 mg, 3.1 mmol), and the solution was stirred 10 min at −78 °C. Then **1b** (936 mg, 2.52 mmol) in dry THF (15 mL) was added dropwise over 15 min, and then the solution was stirred at room temperature for 20 h. The mixture was then diluted with ether and the solution washed with dilute HCl, water, dilute $NaHCO_3$, and saturated NaCl, dried (Na_2SO_4), and evaporated. TLC (10% ethyl acetate–hexane) indicated the presence of mainly (ca 80%) starting material plus one major product band which was isolated by preparative TLC to give 110 mg of a mixture of **3b** (18-Me, δ 0.95) and **4** (18-Me, δ 0.90) (ratio **3b**–**4**, ca. 1:2). Recrystallization from ethanol–ether gave pure **4**: 35 mg; needles; mp 158–160 °C; IR ν 3640, 2240 cm^{-1}; NMR δ 0.90 (s, 3, 18-CH_3), 1.05 (s, 3, 19-CH_3), 1.42 (d, 3, 21-CH_3), 1.1–2.5 (complex m), 2.85 (q, 1, J = 7 Hz, 20-H), 3.5 (m, 2), 3.85 (m, 1), 4.76 (br s, 1, $W_{1/2}$ = 5 Hz, 2′-H), 5.37 (br d, 1, vinyl H); mass spectrum m/e 409 (M − H_2O, 2), 343 (30), 326 (71), 325 (100), 310 (32), 271 (31), 270 (32), 228 (37), 214 (50), 159 (26), 145 (38), 121 (32), 85 (96).

Anal. Calcd for $C_{27}H_{41}NO_3$: C, 75.84; H, 9.66. Found: C, 75.73; H, 9.69.

20-Cyano-3β-tetrahydropyran-2′-yloxypregna-5,17(20)-diene (5a). To a solution of **3b** (2.2 g, 5.91 mmol) in dry benzene (44 mL) and dry pyridine (44 mL) cooled in cold water (5–10 °C) was added thionyl chloride (2.2 g, 18.5 mmol) in dry benzene (44 mL). The solution was slowly heated to reflux (over 30 min) and refluxed for 1 h. After cooling, the solution was added to cold water and extracted with ether. The extract was washed with dilute HCl, 5% $NaHCO_3$, water, and saturated NaCl, dried (Na_2SO_4), and evaporated to yield pure **5a:** 1.98 g (95%); needles from ethanol–ether; mp 160–161 °C (lit.[9] mp 185–194 °C);[14] $[\alpha]^{25}_D$ −9° (c 1.64, $CHCl_3$); IR ν 2200, 1640 cm^{-1}; NMR δ 0.93 (s, 3, 18-CH_3), 1.03 (s, 3, 19-CH_3), 1.83 (slightly br s, 3, 21-CH_3), 3.2–4.2 (br m, 3), 4.73 (br s, 1, $W_{1/2}$ = 7 Hz, 2′-H), 5.36 (br d, 1, J = 4 Hz, vinyl H).

Anal. Calcd for $C_{27}H_{39}NO_2$: C, 79.17; H, 9.60; N, 3.42. Found: C, 78.89; H, 9.61; N, 3.44.

In a similar manner, **3c** (1.0 g, 2.28 mmol) was converted to **3β-*tert*-butyldimethylsilyloxy-20-cyanopregna-5,17(20)-diene (5b)** (890 mg, 93%): blades from ethanol–ether; mp 192–194 °C; IR ν 2200, 1092, 887, 870, 835 cm^{-1}; NMR δ 0.05 (s, 6), 0.90 (s, 9), 0.92 (s, 3, 18-CH_3), 1.02 (s, 3, 19-CH_3), 1.83 (br s, 3, 20-CH_3), 1.1–2.9 (complex m), 3.6 (br m, 1, 3α-H), 5.35 (br d, 1, J = 4 Hz, vinyl H).

Anal. Calcd for $C_{28}H_{45}NOSi$: C, 76.46; H, 10.32; N, 3.19. Found: C, 77.15; H, 10.22; N, 3.02.

20-Cyano-3β-tetrahydropyran-2′-yloxypregn-5-ene (6). Unsaturated nitrile **5a** (5.27 g, 12.8 mmol) was treated with magnesium turnings (25.5 g, 1.05 g-atom) in methanol (260 mL) with stirring at room temperature for 2 h, maintaining the reaction mixture at ca. 25 °C with cooling as required. The progress of the reaction was monitored by taking IR spectra of aliquots extracted with ether and following the change in nitrile absorption (**5a,** ν 2200 cm^{-1}; **6,** ν 2235 cm^{-1}). Additional magnesium (6.4 g, 0.26 g-atom) and methanol (150 mL) were added, and stirring was continued at room temperature for 24 h. Ether was added, and the mixture acidified with cold 6 N HCl, keeping the mixture at ca. 25 °C. Additional ether was added and the extract was washed with saturated $NaHCO_3$, water, and saturated NaCl, dried (Na_2SO_4), and evaporated to yield **6:** 4.77 g (90%); needles from ethanol; mp 148–151 °C; $[\alpha]^{23}_D$ +20° (c 1.08, $CHCl_3$); IR ν 2235, 1209, 1028, 1021 cm^{-1}; NMR δ 0.74 (s, 3, 18-CH_3), 1.02 (s, 3, 19-CH_3), 1.29 (d, J = 7 Hz, 20R-CH_3), 1.33 (d, J = 7 Hz, 20S-CH_3) (ratio of δ 1.29–δ 1.33 ca. 1:2), 1.0–2.4 (complex m), 2.63 (d qu, 1, J_1 = 7 Hz, J_2 = 7 Hz, 20-H), 3.5 (m, 2), 3.9 (m, 1), 4.74 (br s, 1, $W_{1/2}$ = 7 Hz, 2′-H), 5.35 (br d, 1, J = 4 Hz, vinyl H).

Anal. Calcd for $C_{27}H_{41}NO_2$: C, 78.78; H, 10.04; N, 3.40. Found: C, 78.86; H, 10.26; N, 3.53.

3β-Tetrahydropyran-2′-yloxy-23,24-bisnorchol-5-en-22-al (7a). A solution of **6** (400 mg, 0.96 mmol) in dry benzene (8 mL) and heptane (5 mL) at 0 °C under N_2 was treated with a solution of diisobutylaluminum hydride (4 mL, 0.81 M, 3.24 mmol) for 3 h, with spontaneous warming to room temperature. The solution was then poured into ice-cold saturated NH_4Cl and acidified with dilute H_2SO_4. The mixture was extracted with ether, and the extract was washed with saturated $NaHCO_3$ and saturated NaCl, dried (Na_2SO_4), and evaporated to yield a mixture from which **7**, 350 mg (mixture of **7a** + **7b**), was isolated by preparative TLC (30% ethyl acetate–hexane); NMR included singlets at δ 0.68 and 0.72 (ratio ca. 1:2). A portion (25%) of the mixture was recrystallized three times from absolute ethanol giving **7a:** 18 mg; needles; mp 127–129 °C; $[\alpha]^{25}_D$ −39° (c 0.51, $CHCl_3$) (lit.[9] mp 137–139 °C, $[\alpha]_D$ −39°); IR ν 1720, 1025 cm^{-1}; NMR δ 0.72 (s, 3, 18-CH_3), 1.01 (s, 3, 19-CH_3), 1.11 (d, 3, J = 7 Hz, 21-CH_3), 2.35 (d, 2, J = 7 Hz, 7-H_2), 3.5 (m, 2), 3.9 (m, 1), 4.73 (br s, 1, $W_{1/2}$ = 9 Hz, 2′-H), 5.36 (br s, 1, $W_{1/2}$ = 11 Hz, vinyl H), 9.55 (d, 1, J = 3 Hz, CHO). The isomer **7b** was not isolated in pure form.

Anal. Calcd for $C_{27}H_{42}O_3$: C, 78.21; H, 10.21. Found: C, 78.57; H, 10.31.

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Registry No.—**1a,** 53-43-0; **1b,** 19637-35-5; **1c,** 42151-23-5; **3a,** 67464-51-1; (20S)-**3b,** 67464-52-2; (20R)-**3b,** 67464-53-3; **3c,** 67464-54-4; (20S)-**4,** 67504-73-8; (20R)-**4,** 67504-74-9; (*E*)-**5a,** 58449-03-9; (*Z*)-**5a,** 58449-04-0; (*E*)-**5b,** 67488-41-9; (*Z*)-**5b,** 67464-55-5; **6a,** 67464-56-6; **6b,** 67464-57-7; **7a,** 22145-61-5; **7b,** 67488-42-0; *tert*-butyldimethylchlorosilane, 18162-48-6; propionitrile, 107-12-0.

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(1) Address inquiries to this author at the Worcester Foundation for Experimental Biology, Shrewsbury, Mass. 01545.
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(7) The C-19 methyl signal of **3b** was unaffected by the addition of Eu(fod)$_3$. The observed shifts of other signals indicated that complexation with Eu(fod)$_3$ had also occurred with the OTHP functionality. The signals for C-2′–H and C-3 were strongly shifted (from δ 4.73 to 8.7, and from δ 3.85 to 5.8, respectively), as compared with the less pronounced shifts of the C-18 methyl and C-20–H (from δ 2.74 to 3.27) and C-21 methyl (from δ 1.47 to 1.77). In contrast, the C-18 and C-19 methyl signals of cholesterol–OTHP ether were not affected by Eu(fod)$_3$. Thus, the doubling of C-18 methyl signals of **3b** cannot be attributed to the presence of diastereomers formed by the THP ether of **3b.**
(8) The fact that the C-18 methyl signals of both **3b** and **4** are shifted downfield to approximately the same extent by Eu(fod)$_3$ indicates that complexation is not occurring exclusively with the C-17 hydroxyl group.
(9) M. L. Raggio and D. S. Watt, *J. Org. Chem.*, **41,** 1873 (1976).
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(11) J. A. Edwards, J. S. Mills, J. Sundeed, and J. H. Fried, *J. Am. Chem. Soc.*, **91,** 1248 (1969).
(12) For other recently reported methods for the conversion of 17-keto steroids to 17α*H*, 20β*H* side-chain extended steroids, see B. M. Trost and T. R. Verhoeven, *J. Am. Chem. Soc.*, **98,** 630 (1976), and J. Wicha and K. Bal, *J. Chem. Soc., Chem. Commun.*, 968 (1975).
(13) Microbiologically produced **2** has been converted, following the procedure described in this note, in good yields into the 1α-tetrahydropyran-2′-yloxy analogues of **3b, 5a, 6,** and **7.** However, to date only the analogue of **3b** has been obtained in crystalline form (mp 174–175 °C) [D. J. Aberhart and T. Y. Chau, unpublished]. Further work on the application of this approach to the synthesis of 1α-hydroxyvitamin D precursors will be reported in due course.
(14) The large discrepancy in the melting point of this product compared with that of Watt et al.[9] may be the result of a different ratio of 20-*E*/*Z* isomers. The compounds were prepared by different methods.