

cm<sup>-1</sup>; NMR (CDCl<sub>3</sub>) δ 7.95–7.10 (complex m, 18 H), 3.50–1.0 (complex, 12 H).

Anal. Calcd for C<sub>34</sub>H<sub>30</sub>O<sub>2</sub>: C, 86.77; H, 6.43. Found: C, 86.68; H, 6.38.

**C. By Butyric Anhydride.** To a mixture of 0.800 g (6 mmol) of aluminum trichloride and 0.510 g (3.25 mmol) of butyric anhydride in 60 mL of methylene chloride was added dropwise at 0 °C 0.773 g (2.95 mmol) of 11 in 30 mL of methylene chloride under a nitrogen atmosphere. The mixture was allowed to react at room temperature for 16 h. The mixture was poured into cold aqueous hydrochloric acid and extracted with methylene chloride. The organic layer was stirred with sodium bicarbonate and worked up in the usual manner to provide a residue which was chromatographed over silica gel. Elution with hexane afforded 0.38 g of unreacted 11 (1.5 mmol; 50%). Elution with hexane–ethyl acetate (8:2) gave 0.437 g of 17 (1.31 mmol; 45%); mp 61 °C; IR (CHCl<sub>3</sub>) 1680 and 1605 cm<sup>-1</sup>; NMR (CDCl<sub>3</sub>) δ 7.85 and 7.30 (AB quartet, 4 H, *J* = 8 Hz), 7.25 (s, 5 H), 3.5–0.7 (complex, 19 H).

Anal. Calcd for C<sub>24</sub>H<sub>28</sub>O: C, 86.70; H, 8.49; O, 4.89. Found: C, 86.75; H, 8.43; O, 4.82.

Further elution with hexane–ethyl acetate (8:2) furnished 0.050 g of diacyl 18 (0.050 g; 4%); mp 99 °C; IR (CHCl<sub>3</sub>) 1680 and 1605 cm<sup>-1</sup>; NMR (CDCl<sub>3</sub>) δ 7.85 and 7.30 (AB quartet, 8 H, *J* = 8 Hz), 3.5–0.7 (m complex, 26 H).

Anal. Calcd for C<sub>28</sub>H<sub>34</sub>O<sub>2</sub>: C, 83.54; H, 8.51; O, 7.95. Found: C, 83.26; H, 8.43; O, 8.31.

**Mono- and Diacids 19 and 20.** Treatment of 0.41 g (1.3 mmol) of 13 dissolved in 25 mL of dioxane by a solution of 5 g of KOH and 1 mL of bromine in 10 mL of water at 0 °C for 12 h afforded after extraction with methylene chloride 0.40 g of monoacid 19, which was esterified by diazomethane to give 21; mp 93 °C; IR (CHCl<sub>3</sub>) 1720 and 1610 cm<sup>-1</sup>; NMR (CDCl<sub>3</sub>) δ 7.85 and 7.30 (AB quartet, 4 H, *J* = 8 Hz), 7.25 (s, 5 H), 3.30 (s, 3 H).

Anal. Calcd for C<sub>22</sub>H<sub>24</sub>O<sub>2</sub>: C, 82.46; H, 7.55; O, 9.99. Found: C, 82.57; H, 7.49; O, 9.94.

A similar treatment of the diacetyl derivative 15 gave quantitatively the diacid 20 which was converted into the diethyl ester 22; mp 111 °C; IR (CHCl<sub>3</sub>) 1700 and 1610 cm<sup>-1</sup>; NMR (CDCl<sub>3</sub>) δ 7.90 and 7.30 (AB quartet, 8 H, *J* = 8 Hz), 4.35 (q, 4 H), 3-1 (complex, 18 H).

Anal. Calcd for C<sub>26</sub>H<sub>30</sub>O<sub>4</sub>: C, 76.82; H, 7.44; O, 15.74. Found: C, 76.76; H, 7.32; O, 15.92.

**Nitration of Hydrocarbon 11.** To solution of 1 g (3.8 mmol) of hydrocarbon 11 in 24 mL of acetic anhydride was added dropwise at 0 °C a solution of 0.17 mL of fuming nitric acid in 5 mL of acetic anhydride. After the reaction was stirred for 4 h at 20 °C, the mixture was worked up in the standard manner. Chromatography on silica using hexane as eluent afforded successively 0.30 g (1.15 mmol, 30%) of unreacted 11, 0.60 g (2 mmol, 51%) of the mononitro derivative 23, and 0.12 g of a complex unresolved mixture. 23 was crystallized from ethanol; mp 99 °C; IR (CHCl<sub>3</sub>) 1600 and 1350 cm<sup>-1</sup>; NMR (CDCl<sub>3</sub>) δ 8.15 and 7.40 (AB quartet, 4 H, *J* = 8 Hz), 7.28 (s, 5 H), 3.5–1 (m, 12 H).

Anal. Calcd for C<sub>20</sub>H<sub>21</sub>O<sub>2</sub>N: C, 78.14; H, 6.89; N, 4.56. Found: C, 78.10; H, 6.93; N, 4.57.

**Electronic Absorption Spectra.** Ultraviolet spectra were recorded on a Cary Model 15 spectrophotometer using 1-cm cells at 25 °C. All the compounds in the series 11–23 were studied and their absorption spectra were found to be identical with those of the corresponding references (phenylcyclopentane or para-substituted toluenes). Compounds 11, 13, and 23 were examined in the presence of electron acceptors, chloranil and TCNE, in CH<sub>2</sub>Cl<sub>2</sub> at equimolar concentrations of both components (≈10<sup>-2</sup> M) and compared to the spectra of the references recorded in the same conditions. No perturbation was detected.

**Registry No.**—1, 69867-45-4; 2, 69867-46-5; 3, 69867-47-6; 4, 69867-48-7; 5, 69867-49-8; 6, 69867-50-1; 7, 69867-51-2; 8, 69867-52-3; 9, 69867-53-4; 10, 69867-54-5; 11, 69867-55-6; 12, 69867-56-7; 13, 69867-57-8; 14, 69867-58-9; 15, 69867-59-0; 16, 69867-60-3; 17, 69867-61-4; 18, 69867-62-5; 20, 69867-64-7; 21, 69867-65-8; 22, 69867-66-9; 23, 69867-67-0; thionyl chloride, 7719-09-7.

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## Dry Ozonation of Steroids. C-25 Functionalization of Cholestane Derivatives

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The ozonation of substrates adsorbed on dry silica gel is a convenient method to introduce oxygen into unactivated tertiary C–H bonds.<sup>1</sup> This method involves preadsorption of substrate on chromatographic grade silica gel and passing over it ozone at temperatures between –75 and –45 °C, followed by elution with an appropriate solvent. The reactivity of C–H bonds toward ozone depends both on the electronegativity of the C atom and on its steric availability.

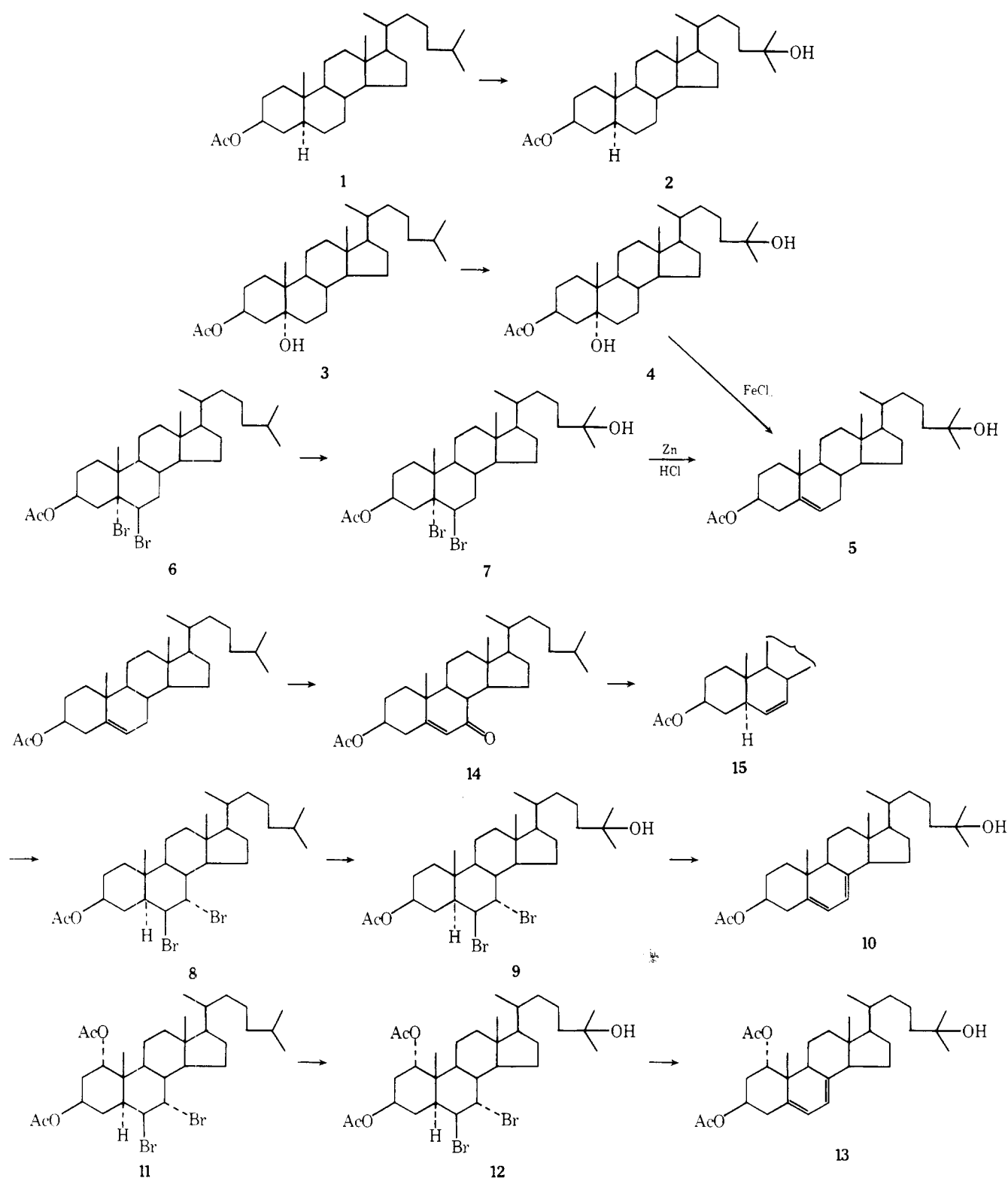
As part of our program to synthesize 25-hydroxycholesterol and its derivatives, we have studied the utilization of ozone as a reagent for the hydroxylation of saturated derivatives of cholesterol as a complimentary method to the previously described<sup>2</sup> peracetic acid oxidation.

We have already published<sup>1d</sup> a preliminary report on dry ozonation of 1α,3β-diacetoxy-6,7-dibromo-5α-cholestane (11), which led to C-25 hydroxylation. In this study, we describe dry ozonation of other saturated cholestane derivatives substituted at positions 5, 6, or 7 which serve as protecting groups for ring B double bonds. We have chosen cholestan-3β-ol acetate (1) as a model compound, which was ozonated on silica at –78 °C, resulting in 74% conversion to a mixture of hydroxylated products from which cholestan-3β,25-diol 3-acetate (2) was isolated in 8% yield; the rest of the material was a mixture of other monohydroxylated and dihydroxylated products.

Ozonation of cholestan-3β,5α-diol 3-acetate (3) under similar conditions resulted in 80% of hydroxylated products, containing 11% of the 25-hydroxy derivative 4. This material was converted to 25-hydroxycholesteryl acetate (5) on treatment with ferric chloride adsorbed on silica gel.<sup>3</sup>

The yield of hydroxylation was higher on ozonation of the 5,6-dibromide 6, leading to 7 (15% yield and 70% conversion). Even better results were achieved with the 6,7-dibromide 8 (prepared from the known cholest-6-en-3β-ol acetate<sup>4</sup> by bromination with iodobenzene dibromide), which on ozonation at –65 °C gave its 25-hydroxy derivative 9 as the only isolated product in 32% yield of the converted material (50%). This compound is a convenient precursor for the preparation of 25-hydroxyvitamin D<sub>3</sub> as its dehydrobromination leads to the respective provitamin, the cholesta-5,7-diene-3β,25-diol (10).

As mentioned above, ozonation of 6,7-dibromide 11, possessing an additional acetoxy function at 1α, also led to sub-



stitution at C-25 to give, as the only product, its 25-hydroxy derivative 12, the precursor of 13.<sup>1d</sup> However, in this case, only 11% of the material reacted, but the yield was the highest achieved among all of the compounds studied.

The ozonations were performed at constant ozone concentration; the silica was saturated with ozone. The decrease in the conversion with the increase of cholestane substitution may be the result of the stronger absorption on silica gel, with the substrate being less available to ozone attack.

Another likely explanation is that ozone molecules are attracted to the electronegative substituents or even bound to them, with the effective concentration of ozone for the attack of the tertiary carbon atom being thus decreased. Ozone in-

teraction with the carbonyl groups has been previously reported,<sup>5</sup> and we also have observed that 5 $\alpha$ ,6 $\alpha$ -epoxycholestan-3 $\beta$ -ol acetate does not react with ozone,<sup>6</sup> the epoxy group probably deactivating the molecule.

The increased yield of the C-25 hydroxylated product in the more highly substituted cholestane derivatives is due to the substituents sterically hindering the approach of ozone to the other tertiary C atoms in the molecule.

#### Experimental Section

<sup>1</sup>H NMR spectra were recorded on a Bruker WH-90 spectrometer using CCl<sub>4</sub> as a solvent and cyclohexane-*d*<sub>12</sub> as an internal lock. All chemical shifts are reported in  $\delta$  values to tetramethylsilane standard.

The ultraviolet spectra were taken on a Cary 118 spectrophotometer, using ether as a solvent. Mass spectra were recorded on Varian MAT 731 high-resolution mass spectrometer.

**Ozonation of Cholestan-3 $\beta$ -ol Acetate (1).** A solution of the title compound (5.0 g) in pentane (100 mL) was mixed with chromatographic grade silica gel (400 g). The solvent was evaporated in a rotatory evaporator, the dry powder was ozonated for 2 h at  $-78^{\circ}\text{C}$ , and the reaction mixture was extracted with ethyl acetate (500 mL). Chromatography on silica gel (500 g) using ether–methylene chloride (8:92) gave the starting material (1.3 g) and cholestan-3 $\beta$ ,25-diol 3-acetate (2)<sup>2b</sup> (0.285 g); mp 126–127  $^{\circ}\text{C}$ ; NMR  $\delta$  0.67 (s, 3 H, C-18), 0.87 (s, 3 H, C-19), 1.22 (s, 6 H, C-26,27), 2.03 (s, 3 H, OAc); MS *m/e* 446 ( $\text{M}^+$ ). The remaining more polar products were not separated.

**Ozonation of Cholestan-3 $\beta$ ,5 $\alpha$ -diol 3-Acetate (3).** The title compound (1.0 g) dissolved in methylene chloride (100 mL) was adsorbed on silica gel (75 g) as described above and ozonated at  $-78^{\circ}\text{C}$  for 3 h. After being warmed to room temperature, the organic material was eluted with methanol (200 mL). The residue, after evaporation of the solvent, was chromatographed on a column of silica gel (100 g) with a mixture of ether–methylene chloride (93:7) to give the starting material (0.14 g) and cholestan-3 $\beta$ ,5 $\alpha$ ,25-triol 3-acetate (4)<sup>2b</sup> (0.093 g); mp 180–182  $^{\circ}\text{C}$ ; NMR  $\delta$  0.67 (s, 3 H, C-18), 0.9 (d,  $J = 5\text{ Hz}$ , 3 H, C-21), 1.00 (s, 3 H, C-19), 1.20 (s, 6 H, C-26,27), 2.02 (s, 3 H, OAc); MS *m/e* 462 ( $\text{M}^+$ ). The remaining more polar products were not separated.

**Ozonation of 5,6-Dibromocholestan-3 $\beta$ -ol Acetate (6).** The title compound (2 g) dissolved in methylene chloride (100 mL) was adsorbed on silica gel (100 g) as described above and ozonated at  $-78^{\circ}\text{C}$  for 3 h, and the material was eluted with ethyl acetate (500 mL). The solvent was evaporated, and the residue was dissolved in ether (50 mL), treated with zinc powder (0.5 g) and acetic acid (2 mL), and stirred at room temperature for 3 h. The reaction mixture was treated with ether (200 mL) and water (100 mL) and decanted, and the zinc was washed with ether (50 mL). The ether extracts were washed with water and dilute hydrochloric acid and evaporated to dryness to give an oily residue (1.18 g). Chromatography on silica gel (100 g) using methylene chloride–ether (95:5) gave the starting material (0.38 g) and 25-hydroxycholesterol acetate<sup>7</sup> (5; 0.12 g); mp 138–139  $^{\circ}\text{C}$ ; NMR  $\delta$  0.68 (s, 3 H, C-18), 1.02 (s, 3 H, C-19), 1.20 (s, 3 H, C-26,27), 2.03 (s, 3 H, OAc).

**Preparation of 6 $\beta$ ,7 $\alpha$ -Dibromocholestan-3 $\beta$ -ol Acetate. (a) 7-Oxocholest-5-en-3 $\beta$ -ol Acetate (14).<sup>8</sup> Cholesterol acetate (5 g) dissolved in anhydrous *tert*-butyl alcohol (500 mL) was treated with mercuric dibromide (5 g) and anhydrous sodium acetate (2.5 g). The mixture was irradiated with an external light source (Rayonet) of 254 nm at room temperature in an open quartz vessel for 10 h. The solution was filtered, and the filtrate was diluted with hexane (500 mL), extracted five times with water (100 mL), and then evaporated to dryness. The residue was chromatographed on silica gel (500 g) with hexane–ether (9:1), resulting in 5 $\alpha$ ,6 $\alpha$ -epoxycholestan-3 $\beta$ -ol acetate (0.3 g). Elution with hexane–ether (4:1) gave the title compound (3 g), mp 156–158  $^{\circ}\text{C}$ , identical with an authentic sample.**

(b) Cholest-6-en-3 $\beta$ -ol Acetate (15).<sup>4</sup> Diborane was passed through a solution of the enone (3 g) in diethylene glycol dimethyl ether (60 mL) for an hour at room temperature. The reaction mixture was stirred for 40 min and then treated with acetic anhydride (30 mL) and heated under reflux for 1 h. The solution was concentrated under vacuum, and the residue was extracted with ether and washed with water and a solution of 10% sodium hydroxide. Evaporation led to a residue which was chromatographed on neutral alumina (activity 1) with hexane to give the title compound (2.25 g), mp 100–105  $^{\circ}\text{C}$ , identical with an authentic sample:<sup>4</sup> NMR  $\delta$  0.68 (s, 3 H, C-18), 0.90 (s, 3 H, C-19), 2.03 (s, 3 H, OAc), 5.21, 5.61 (AB,  $J = 10\text{ Hz}$ , 2 H, C-6,7).

(c) 6 $\beta$ ,7 $\alpha$ -Dibromocholestan-3 $\beta$ -ol Acetate (8). To a cold and stirred solution ( $-5^{\circ}\text{C}$ ) of cholest-6-en-3 $\beta$ -ol acetate (1 g) in dry hexane (25 mL) was added iodobenzene dibromide in hexane (prepared by addition of bromine (4.8 g) to a solution of iodobenzene (7 g) in dry hexane (10 mL) at room temperature) dropwise. The light yellow reaction mixture was filtered and evaporated to dryness. The residue was chromatographed on silica gel (100 g) with hexane–ether (4:1) to give the title compound (1.2 g); mp 76–77  $^{\circ}\text{C}$ ; NMR  $\delta$  0.72 (s, 3 H, C-18), 0.86 (d,  $J = 6\text{ Hz}$ , 6 H, C-26,27), 1.11 (s, 3 H, C-19A), 2.03 (s, 3 H, OAc), 4.55 (m, 2 H, C-6,7); MS *m/e* 588.1989 ( $\text{M}^+$ ); calculated for  $\text{C}_{29}\text{H}_{48}\text{O}_2^{79}\text{Br}_2$ , 588.2000.

**Ozonation of 6 $\beta$ ,7 $\alpha$ -Dibromocholestan-3 $\beta$ -ol Acetate (9).** The title compound (1 g) was dissolved in hexane (100 mL), adsorbed on silica gel (100 g), and ozonated at  $-65^{\circ}\text{C}$  for 4 h. The excess of ozone was driven off by argon, and the material was eluted with a mixture of ethyl acetate–methanol (4:1). Chromatography on silica gel (100

g) using methylene chloride–ether (4:1) gave the starting material (0.5 g) and 0.16 g of 6 $\beta$ ,7 $\alpha$ -dibromocholestan-3 $\beta$ ,25-diol 3-acetate (9); mp 84–85  $^{\circ}\text{C}$ ; NMR  $\delta$  0.73 (s, 3 H, C-18), 1.12 (s, 3 H, C-19), 1.21 (s, 6 H, C-26,27), 2.03 (s, 3 H, OAc), 4.55 (m, 2 H, C-6,7); MS *m/e* 584.1910 ( $\text{M}^+ - \text{H}_2\text{O}$ ); calculated for  $\text{C}_{29}\text{H}_{46}\text{O}_2^{79}\text{Br}_2$ , 584.1864. The remaining more polar products were not separated.

**25-Hydroxycholesta-5,7-dien-3 $\beta$ -ol Acetate (10).** 25-Hydroxy derivative 9 (14 mg) was dissolved in trifluoroacetic anhydride (1 mL) and left at room temperature for 4 h. The solution was evaporated to dryness under vacuum as the residue was dissolved in hexamethylphosphoramide (10 mL) to which triethylmethylammonium dimethyl phosphate (0.5 mg) was added. The reaction mixture was heated at 135  $^{\circ}\text{C}$  for 2 h under nitrogen. Extraction with ether followed by washing with water and drying of the ether extract with  $\text{MgSO}_4$  resulted in the title compound 10 (5 mg);<sup>9</sup> UV  $\lambda_{\text{max}}$  262, 272, 282, 284 nm. This compound was converted without purification to 25-hydroxyvitamin D<sub>3</sub> by irradiation in ether solution followed by heating for 1 h at 75  $^{\circ}\text{C}$  in isoctane.<sup>10</sup>

**Registry No.**—1, 1255-88-5; 2, 2550-91-6; 3, 1256-33-3; 4, 52092-66-7; 6, 514-50-1; 8, 69707-03-5; 9, 69707-04-6; 10, 24281-78-5; 14, 809-51-8; 15, 987-53-1; 25-hydroxycholesterol acetate, 10525-22-1; cholesterol acetate, 604-35-3; 5 $\alpha$ ,6 $\alpha$ -epoxycholestan-3 $\beta$ -ol acetate, 4092-57-3; 25-hydroxyvitamin D<sub>2</sub>, 19356-17-3.

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## One-Step Synthesis of Uranediol by Reaction of Dichlorobis(benzonitrile)palladium(II) with 5 $\alpha$ -Pregnane-3 $\beta$ ,20 $\beta$ -diol

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Uranediol (17 $\alpha$ -methyl-*D*-homo-5 $\alpha$ -androstane-3 $\beta$ ,17 $\alpha$  $\beta$ -diol) is a homosteroid hormone with androgenic and anabolic properties isolated from the urine of pregnant mares.<sup>1</sup> The structure of the compound has been determined<sup>2</sup> and the synthesis accomplished.<sup>3</sup>

During our investigations on the reactions of sterols and epoxysteroids with  $\text{Pd}(\text{PhCN})_2\text{Cl}_2$ ,<sup>4</sup> we have found that the complex promotes the direct conversion of 5 $\alpha$ -pregnane-3 $\beta$ ,20 $\beta$ -diol (1) into uranediol (2). The reaction occurs in ni-

