Table III. 2-Phenylbenzoxazole[a] Recycling

quencher (concn, mol L^{-1})	recovd 2-phenyl-benzoxazole after 80 cycles, %	global yield after cycle, %	theoretical no. of cycles
none	100 (not irradiated)		
none	90.1	99.87	1770
pyrene (3.5×10^{-3})	93.8	99.92	2880

[a] [2-Phenylbenzoxazole] = 0.1 M in all cases.

Heavy-Atom Effect. Xenon was purchased from "L'air Liquide". Cyclohexane solutions of 2-phenylbenzoxazole were first bubbled with xenon. After three freeze–pump–thaw cycles, the tubes were sealed under 1 atm of xenon. For the irradiated 10^{-1} M solution of 2-phenybenzoxazole, the precipitate was filtered off, washed, and dried as described earlier. For the irradiated 10^{-2} M solution, the recovered 2-phenylbenzoxazole and the photoproducts were measured by VPC with pyrene as an internal standard.

Recycling Capacity of the Chemical Components. The irradiations of 10^{-1} M solutions of 1 were carried out for 2 h by following the general procedure. The average conversion was about 50%. The thermally induced reversion was then performed at 70 °C. Eighty photothermal cycles were achieved under these conditions. The same procedure was repeated after adding a cyclohexane solution of pyrene (3.5×10^{-3}M) to the solution of the dimer. The quantity of 2-phenylbenzoxazole recovered in these experiments was compared to the initial quantity of 2-phenylbenzoxazole. These measurements were performed by VPC analysis after adding the same quantity of pyrene to each sample. The chemical yield of starting material recovered after one cycle (and then the maximal number of cycles) was calculated from the yield of 2-phenylbenzoxazole unchanged after 80 cycles (Table III). The total energy converted after 2880 cycles was determined by computing the energy released for each cycle, the latter decreasing as the formation of byproducts increases.

Thermodynamic Measurements. The thermally induced reversion of 2 → 1 was studied by following the increase of absorbance of a cyclohexane solution of 2 (1 mg of 2 dissolved in 100 mL of solvent) by using a constant temperature bath (Figure 2). The first-order rate constant was determined by using the least-squares Guggenheim method[31-33] on a Tektronix 4051 microcomputer. In the kinetic measurements, the infinity spectrum agreed with that of authentic 2-phenylbenzoxazole. The effect of temperature was determined by obtaining the rate constant at various temperatures. The activation energy (E_a) and the preexponential factor (A) were derived from the Arrhenius equation $\ln K = \ln A - E_a/RT$ (correlation coefficient ≤ 0.997).

Microcalorimetric Measurements. Microcalorimetric measurements were carried out in an L.K.B. 8700-1 calorimeter with 100-mL cells. The dissolution reaction of Tris (tris(hydroxymethyl)aminomethane)[34] in a 0.1 M HCl solution was used for calibration. The data were treated as described in Wadso's original paper.[35] Molar enthalpies were obtained with benzene as the solvent. The benzene was dried by passing it through a column of 3-Å molecular sieves and stored over molecular sieves of the same pore size. Samples were weighed on a Mettler balance with an accuracy of 1×10^{-6} g. The cells were filled and sealed under a dry inert atmosphere.

Acknowledgment. We thank Prof. Reisse for allowing us to perform the microcalorimetric measurements in his laboratory at the University of Brussels.

Registry No. 1, 833-50-1; 2, 82461-25-4; cyclohexane, 110-82-7.

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Transformations of Cyclopropanol Intermediates. 5. Preparation and Reactions of 1-Hydroxy-1,5α-cyclocholestan-7-one

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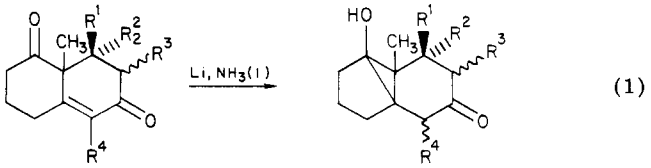
Cholest-5-ene-1,7-dione, a new polyfunctional steroid, gave 1-hydroxy-1,5α-cyclocholestan-7-one (6) on dissolving metal reduction. Acid- and base-catalyzed isomerizations of 6 were studied and the results compared with corresponding reactions of the parent cyclopropanol 1a. The chief rearrangement products from 6 were the cis and trans 1,7-diketo steroids 10 and 11 and the ring-A spiro epimers 12 and 13. Surprisingly, no B-norsteroid products were obtained despite the isolation of an isomer of 6, 7-hydroxy-5,7β-cyclocholestan-1-one (14), from the base-induced reaction of 6. Ring-cleavage reactions of reduced derivatives of 6 and 14 were also examined.

Dissolving metal reduction of the Wieland–Miescher ketone and several methyl homologues thereof invariably gives cyclopropanols having structure 1 (eq 1).[1] The



(1)

1a, R^{1-4} = H
b, R^1 = CH_3; R^{2-4} = H
c, R^2 = CH_3; $R^{1,3,4}$ = H
d, R^3 = CH_3; $R^{1,2}$ = H
e, R^4 = CH_3; R^{1-3} = H

course of acid- and base-catalyzed ring-opening reactions of these cyclopropanols is sensitive to the location and orientation of substituents.[2] For example, reaction of the parent system 1a with potassium hydroxide in aqueous methanol gave a mixture of the isomeric bicyclic diketones 2a, 3a, and 4a, whereas the analogous 7-methyl epimers 1b and 1c were transformed under similar conditions with remarkable selectivity (eq 2).

To explore the course of these synthetic transformations

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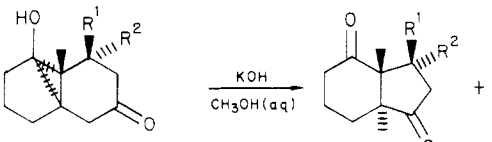
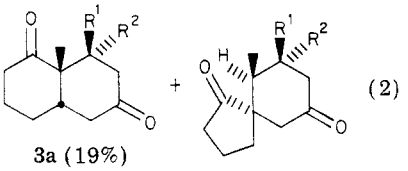


1a, $R^1 = R^2 = H$
b, $R^1 = CH_3$; $R^2 = H$
c, $R^1 = H$; $R^2 = CH_3$

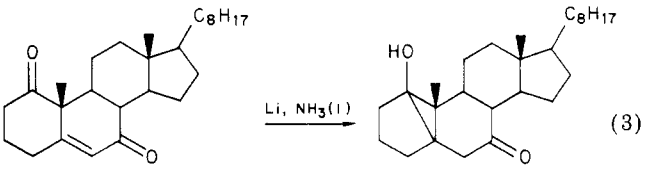
2a (80%)
2b (90%)



3a (19%)
3c (99%)
4a (trace)

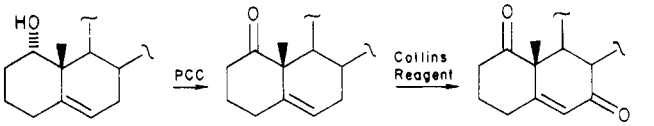
(2)

in more complex systems, we have prepared a 1,5-cyclosterol analogue of 1 and subjected it to acid- and base-catalyzed isomerization. A new polyfunctional cholestane, 5, served as the precursor of the desired cyclosterol, 6, as shown in eq 3.



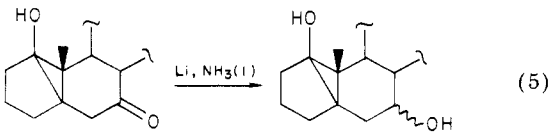
5 6 (3)

Our synthesis of 5 began with 1α-hydroxycholest-5-ene (7), prepared according to Okamura.[3] This crystalline substance proved to be a mixture of Δ^5- and Δ^4-isomers (roughly 3:1). Oxidation of 7 by PCC or PDC gave unsaturated ketone 8, as an equivalent mixture of Δ^5- and Δ^4-isomers. Allylic oxidation of 8 by excess Collins reagent[4] then gave a modest yield of 5, accompanied by unreacted 8 and tarry byproducts. By recyling recovered 8, we obtained 5 in 30% yield from 7 (eq 4).



7 8 5 (4)

Dissolving metal reduction of 5 by lithium in ammonia/THF gave cyclosterol 6 in over 85% yield. Subsequent reduction of 6 by lithium in ammonia yielded diol 9, which was used without purification in a parallel series of acid- and base-catalyzed isomerizations (eq 5). The only structural characterization made for 9 was the absence of carbonyl stretching absorption in its infrared spectrum.



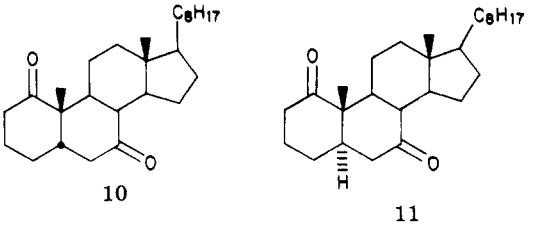
6 9 (5)

In the remainder of this report we describe acid- and base-catalyzed reactions of 6 and 9 and compare these results with those reported for the parent system 1a.[2] Since the cis and trans diketones 10 and 11 are potential products of these reactions, they were prepared independently by catalytic reduction of 5, the resulting mixture being separated easily by chromatography. The trans isomer 11 is a known compound,[5] but the cis isomer 10 is described here for the first time. The physical properties of 10, and all other new compounds reported here, are described in the Experimental Section and support the assigned structures. Table I lists the chief products from prolonged acid (hydrochloric acid in THF) and base (aqueous potassium hydroxide in THF) treatment of 6. They include 10, 11, and a difficultly separable mixture of epimeric spirodiketones 12 and 13.

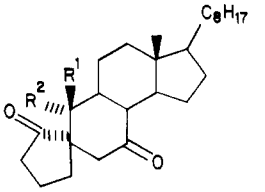
Table I. Acid- and Base-Catalyzed Reactions of Cyclosterols 6 and 9

substrate	reaction conditions	products[a]
6	HCl, THF, 25 °C, 6 h	10 (13%) + 11 (38%) + 12 and 13 (25%)
9	1. HCl, THF, 25 °C, 12 h 2. Jones oxidation	10 (trace) + 11 (trace) + 12 and 13 (78%)
6	KOH, THF/CH_3OH,	10 (66%) + 11 (trace) + 12 and 13 (16%)
9	1. KOH, THF/CH_3OH, 25 °C, 12 h 2. Jones oxidation	10 (16%) + 11 (trace) + 12 and 13 (30%)

[a] In all cases the ratio of 12 to 13 was 70:30.



10 11



12, $R^1 = CH_3$; $R^2 = H$
13, $R^1 = H$; $R^2 = CH_3$

The product distributions shown in Table I indicate that cyclosterols 6 and 9 undergo acid- and base-catalyzed ring-opening isomerizations comparable to those reported earlier for 1 and its derivatives.[2] In particular, removal of the homo-conjugated carbonyl function (as in 9) changes the regioselectivity of these isomerizations in similar ways. However, two interesting differences between the reactions of 6 and 1 may be noted. First, the stereoselectivity of the C-protonation stage is much poorer in the ring-opening reactions of 6 (and 9) than in equivalent reactions of 1. For example, spiro[4.5]decane products such as 4 are formed from 1, or its reduced derivative, with exclusive retention of configuration,[2,6] but 12 and 13 appear to be formed together in roughly 70:30 ratio from both acid- and base-catalyzed reactions of 6 and 9. The major epimer 12, has been assigned the axial methyl configuration (retention of configuration) on the strength of the chemical shift dif-

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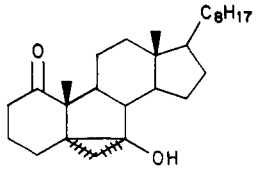
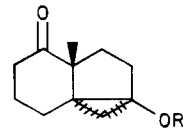
ference observed for the methyl doublets: **12** (1.145 ppm, J 7.0 Hz), **13** (0.935 ppm, J = 6.9 Hz). In this rigid steroid framework an axial methyl group at C-10 is deshielded by a carbonyl function at C-7[7] (assuming ring B adopts a chair conformation). Acid-catalyzed isomerization of **6** also generates a larger amount of the trans decalin **11** than was observed in the earlier study of **1**.

A second difference between the reactions of **6** and **1** is the absence of a B-norsteroid product, equivalent to **2** in the parent system, among the tetracyclic isomers obtained from **6**. A comparison with **1b** is particularly striking in that **2b** is the exclusive product of its base-catalyzed isomerization (eq 2). This difference became even more surprising when we discovered that mild base treatment of **6** gave the isomeric cyclopropanol **14** in 23% yield,



14



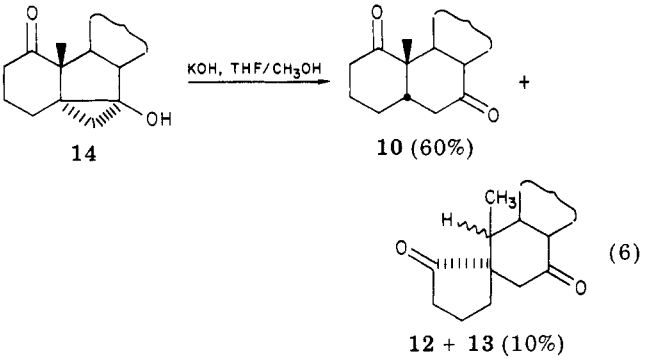
15a, R = H
b, R = $COCH_3$

together with **10** (10%), **12** + **13** (5%), and recovered **6** (33%). A rearrangement cyclopropanol of this kind (i.e., **15a**) has been proposed as an intermediate in the conversion of **1a** into **2a**; indeed, an acetate derivative (**15b**) was transformed to **2a** completely and rapidly on treatment with base.[2]

Compound **14** was purified by chromatography on silica gel and proved to be a moderately stable crystalline solid, mp 92–94 °C, having spectroscopic properties commensurate with the assigned structure. The configuration of this 5,7-cyclosterol was assigned by comparing the ^1H NMR signals of the 19-methyl, 6β, and 6α protons with the corresponding signals reported for other 5,7β-cyclosteroids[9] and their 5,7α-isomers.[9a] For example, the cyclopropane moiety in a group of authentic 5,7β-cyclosteroids induces a 0.09 ± 0.02 ppm (downfield) shift of the 19-angular methyl group, according to the additive approach described by Zurcher.[8] A similar analysis of two 5,7α-cyclosteroids reported by Joska et al.[9a] indicates that this configurationally isomeric cyclopropane moiety causes a −0.22 ± 0.03 ppm (upfield) shift of the 19-methyl signal. In both of these computations we used the 5α-cholestane system as a reference, since it more closely approximates the shape of both the 5,7α- and 5,7β-cyclosteroids than does 5β-cholestane. The cyclosteroid increments thus obtained were then used to calculate the 19-methyl chemical shift in compound **14**, and this value, 1.26 ppm, agreed well with the observed shift, 1.25 ppm.

The geminal cyclopropyl protons in **14** appear as broad doublets at 0.23 and 1.00 ppm, J = 5.57 Hz, in its ^1H NMR spectrum. Some long-range coupling is apparent on close inspection of these signals, and a model suggests that protons at C-8 and C-4(β) are ideally oriented for coupling with 6β and 6α, respectively. Finally, we note that the relatively small chemical shift (0.23 ppm) associated with one of the cyclopropyl protons, presumably 6β, corresponds to observations made the authentic 5,7β-cyclosteroids.[9] The isomeric 5,7α-cyclosteroids do not exhibit any ^1H NMR signals at higher field than the 18-methyl singlet (ca. 0.70 ppm).[9a]

Treatment of **14** with potassium hydroxide in a THF/MeOH solution yielded a mixture of **10**, **12** and **13** (eq 6)



14 **10** (60%) (6)

12 + **13** (10%)

similar to that obtained from **6** (Table I). It is clear that **6** and **14** must be interconverted under these reaction conditions, but the failure of the latter to isomerize to a B-norsteroid remains unexplained. Such a product would be formed initially in a trans, anti, trans configuration of rings A, B, and C, and this appears to be more strained than the normal steroid ring system. Consequently it is possible that reaction of **14** by cleavage of the 6, 7 bond is less favorable than the comparable reaction of **15a**. In this respect we were particularly surprised to find that preliminary reduction of **14** (Li in NH_3) followed by base treatment and oxidation gave **10** as the only product. Since our sample of **14** was very small at this point, we did not characterize the initial reduction product. Nevertheless, the tendency of 5,7β-cyclosterol **14** and its 1-ol derivative to react by cleavage of the 5,7 bond, with retention of configuration at C-5, is demonstrated unequivocally.

Experimental Section

IR spectra were recorded on a Perkin-Elmer 237B grating spectrophotometer. ^1H NMR spectra were taken in $CDCl_3$ solution on either a Varian T-60 or a Bruker 250 MHz spectrometer and are calibrated in ppm downfield from Me_4Si as an internal standard. ^{13}C NMR spectra were obtained with a Varian CFT-20 spectrometer or with the Bruker 250-MHz instrument. Mass spectra were taken with a Finnigan 4000 GC/MS spectrometer or, in the case of high-resolution measurements, with a Varian MAT CH-5DF spectrometer. UV spectra were recorded on a Unicam SP-800 spectrophotometer. Melting points were measured on either a Hoover-Thomas apparatus (capillary tube) or on a Reichert hot-stage microscope and are uncorrected.

Microanalyses of C and H were performed by Spang Microanalytical Laboratories, Eagle Harbor, MI.

All reactions in which strongly basic reagents were used were conducted under N_2 or argon, with solvents purified by distillation from suitable drying agents in the absence of O_2.

Cholest-5-en-1-one (8). To a stirred slurry of 1.05 g (4.9 mmol) of pyridinium chlorochromate in 3 mL of methylene chloride was added a solution of 1.0 g (2.59 mmol) of 1α-hydroxycholest-5-ene (**7**)[3] in 2 mL of methylene chloride. This mixture was stirred for 2 h, diluted with 20 mL of ether, and decanted. The black precipitate was washed with ether, and the combined extracts were filtered through a layer of florisil. Evaporation of the clear solution gave 0.8 g of yellow oil, which crystallized from an acetone/methanol solution, yielding 0.72 g (72%) of **8**, mp 97–101 °C. This mixture of Δ^5- and Δ^4-isomers (ca. 70:30) exhibit the following properties: IR ($CHCl_3$) 1700 cm^{-1}; ^1H NMR ($CDCl_3$) 0.677 (s, 3 H, C-18), 0.862 (d, 3 H, J = 6.6 Hz), 0.365 (d, 3 H, J 6.6 Hz), 0.911 (d, 3 H, J = 6.6 Hz, C-21), 1.266 (s, 3 H, C-19), 5.50 (br s, 1 H) ppm; mass spectrum (70 eV), m/e (relative intensity) 384 (100), 369 (15), 271 (17), 176 (45), 124 (47). Anal. Calcd for $C_{27}H_{44}O$: C, 84.31; H, 11.53. Found: C, 84.08; H, 11.61.

Cholest-5-ene-1,7-dione (5). To a cold (0 °C) solution of 25 g of pyridine in 300 mL of methylene chloride was added with stirring 15 g (0.15 mmol) of chromium trioxide. The resulting

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(9) (a) J. Joska, J. Fajkos, and F. Sorm, *Collect. Czech. Chem. Commun.*, **33**, 2049 (1968); (b) J. Fajkos, M. Budesinsky, and J. Joska, *ibid.*, **38**, 1406 (1973); (c) P. Gassman and W. Hymans, *Tetrahedron*, *24*, 4437 (1968).

burgundy-colored solution was slowly warmed to room temperature, following which a solution of 4 g (0.01 mol) of **8** in 3 mL of methylene chloride was added in one portion. After 24 h of stirring at room temperature, a second portion of the chromium trioxide–pyridine complex (prepared from 7.5 g of CrO_3) was added, and the oxidation was continued an additional 48 h. This reaction mixture was decanted, the tarry precipitate was washed with three 150-mL portions of methylene chloride, and the combined organic solutions were evaporated to afford a dark oil which was dissolved in 500 mL of ether. This filtered ether solution was washed with 150-mL portions of 5% hydrochloric acid, water, and brine before being dried over magnesium sulfate. Evaporation of the solvent and chromatography of the resulting solid (silica gel, 35% ethyl acetate/hexane) gave 200 mg of recovered **8** and 800 mg (25%) of **5**. Crystallization of **5** from methanol gave a solid: mp 81–82 °C; IR ($CHCl_3$) 1715, 1650 cm^{-1}; ^1H NMR ($CDCl_3$) 0.689 (s, 3 H, C-18), 0.860 (d, 3 H, J = 6.7 Hz), 0.863 (d, 3 H, J = 6.6 Hz), 0.915 (d, 3 H, J = 6.6 Hz, C-21), 1.419 (s, 3 H, C-19), 5.803 (d, 1 H, J = 1.4 Hz) ppm; ^{13}C NMR ($CDCl_3$) 200.38, 196.92, 163.99, 126.1 0, 54.98, 50.36, 45.12, 43.39, 43.24, 39.49, 38.75, 37.01, 36.21, 35.65, 30.48, 28.46, 27.93, 26.18, 23.87, 23.18, 22.77, 22.53, 18.88, 16.65, 12.12 ppm.; mass spectrum (70 eV), m/e (relative intensity) 398 (2), 380 (22), 342 (50), 55 (100). Anal. Calcd for $C_{27}H_{42}O_2$: C, 81.35; H, 10.62. Found: C, 81.10; H, 10.70.

1-Hydroxy-1,5α-cyclocholestan-7-one (6). To a cold (−78 °C) solution of 30 mg (4.2 mmol) of lithium metal in 30 mL of ammonia (freshly distilled from sodium) and 5 mL dry THF was added dropwise a solution of **5** (300 mg, 0.75 mmol) in 4 mL of THF. Following 30 min of stirring, the reaction mixture was quenched with 1.0 g of ammonium chloride and the solvents were evaporated under a stream of nitrogen. The residue was dissolved in ether, washed with water and brine, and dried over sodium sulfate. Evaporation yield 267 mg (89%) of crude **6**, which was used without purification for subsequent studies. TLC and ^1H NMR analyses indicated that this crude product was contaminated by a small amount (ca. 5%) of unreacted **5**. An analytical sample of **6** was prepared by crystallization from acetone: mp 113–118 °C; IR ($CHCl_3$) 3350, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) 0.718 (s, 3 H, C-18), 0.856 (d, 3 H, J = 6.4 Hz), 0.860 (d, 3 H, J = 6.8 Hz), 0.915 (d, 3 H, J = 6.4 Hz), 0.928 (s, 3 H, C-19) ppm; ^{13}C NMR (benzene-d_6) 194.46, 71.28, 55.60, 52.03, 47.36, 43.70, 40.04, 39.87, 39.54, 39.16, 36.60, 36.20, 33.92, 33.44, 32.33, 30.67, 28.56, 28.45, 26.03, 24.74, 24.31, 23.37, 23.02, 22.78, 19.14, 11.97, 8.27 ppm; mass spectrum (70 eV), m/e (relative intensity) 400 (15), 382 (10), 151 (65), 124 (100). Anal. Calcd for $C_{27}H_{44}O_2$: C, 80.94; H, 11.07. Found: C, 81.23; H, 10.92.

5β-Cholestane-1,7-dione (10) and 5α-Cholestane-1,7-dione (11). A solution of 50 mg (0.13 mmol) of **5** in 3.5 mL of ethyl acetate was hydrogenated over a palladium catalyst (10% Pd/C) for 20 h (1 atm H_2). This solution was filtered and evaporated to give 50 mg of an oil, which on chromatography (silica gel, 25% ethyl acetate/hexane) yielded 18 mg (36%) of **10** and 28 mg (56%) of **11**. Crystallization of each from 95% ethanol gave **10**, mp 110–111 °C (lit.[5] mp 110–111 °C), and **11**, mp 148–148.5 °C. Other properties of **11** are as follows: IR 1705 cm^{-1}; ^1H NMR ($CDCl_3$) 0.645 (s, 3 H, C-18), 0.857 (d, 3 H, J = 6.6 Hz), 0.862 (d, 3 H, J = 6.6 Hz), 0.889 (d, 3 H, J 6.7 Hz), 1.401 (s, 3 H, C-19) ppm; mass spectrum (70 eV), m/e (relative intensity) 400 (10), 382 (2), 111 (30), 43 (100). Anal. Calcd for $C_{27}H_{44}O_2$: C, 80.94; H, 11.07. Found: C, 81.17, H, 11.08.

Acid-Catalyzed Reactions of Cyclopropanol 6. A solution of 60 mg (0.15 mmol) of **6** in 4 mL of tetrahydrofuran (THF) containing 4 drops of concentrated hydrochloric acid was stirred for 6 h at room temperature. The reaction mixture was diluted with either, washed with sodium bicarbonate solution, and dried. Evaporation of the solvent followed by chromatography of the resulting oil (silica gel, 25% ethyl acetate/hexane) gave 8 mg (13%) of **10**, 23 mg (38%) of **11**, 15 mg (25%) of a mixture of **12** and **13** (70:30), mp 121–128 °C, and 3 mg (5%) of **5**. The mixture of **12** and **13** exhibited the following properties: IR ($CHCl_3$) 1710, 1760 cm^{-1}; ^1H NMR ($CDCl_3$) 0.656 (s, 3 H, C-18, **12**), 0.664 (s, 3 H, C-18, **13**), 0.859 (d, 3 H, J = 6.6 Hz, **12** and **13**), 0.864 (d, 3 H, J = 6.7 Hz, **12** and **13**), 0.906 (d, 3 H, J = 6.6 Hz, **12** and **13**), 0.936 (d, 3 H, J = 6.9 Hz, C-19 in **13**), 1.146 (d, 3 H, J = 7.0 Hz, C-19 in **12**); mass spectrum (70 eV), m/e (relative intensity) 400 (10), 382 (9), 290 (20), 111 (30), 55 (48), 43 (100).

Base-Catalyzed Reactions of 6. To a solution of 60 mg (0.15 mmol) of **6** in 4 mL of THF at 0 °C was added 0.35 mL of a solution of 0.35 g (6.3 mmol) of potassium hydroxide in 8 mL of deoxygenated 1:1 methanol/water. This solution was stirred for 2 h at 0 °C and then overnight at room temperature. After dilution with ether, the organic layer was washed with water and brine and then dried . Evaporation of the solvent followed by chromatograhy of the crude product on silica gel gave 40 mg (66%) of **10**, 10 mg (16%) of **12** and **13** (70:30), and 3 mg of **5**.

7-Hydroxy-5,7β-cyclocholestan-1-one (14). To a stirred solution of 60 mg (0.15 mmol) of **6** in 4 mL of THF was added 0.35 mL (0.45 mmol) of the same potassium hydroxide solution used in the previous experiment. The progress of this reaction was followed by TLC (silica gel) analysis. After 5 h the reaction mixixture was diluted with ether, washed with water and brine, and dried over sodium sulfate. Evaporation of the solvent, followed by chromatography (silica gel), gave 6 mg (10%) of **10**, 20 mg of recovered **6**, 3 mg (5%) of **12** and **13**, 3 mg of **5**, and 14 mg (23%) of **14**, mp 92–94 °C. This crystalline solid exhibited the following properties: IR 3350, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) 0.229 (d, 1 H, J = 5.6 Hz), 0.673 (s, 3 H, C-18), 0.863 (d, 3 H, J = 6.5 Hz), 0.879 (d, 3 H, J = 6.7 Hz), 0.915 (d, 3 H, J = 6.6 Hz), 0.996 (d, 1 H, J = 5.6 Hz), 1.245 (s, 3 H, C-19); mass spectrum (70 eV), m/e (relative intensity) 400 (11), 385 (8), 151 (30), 124 (35), 55 (60), 43 (100); molecular ion mass 400.33337, calcd for $C_{27}H_{44}O_2$ 400.33413.

1-Hydroxy-1,5α-cyclocholestan-7-ol (9). A solution of 200 mg (0.5 mmol) of **6** in 15 mL of THF was added to a cold (−78 °C) solution of 28 mg (4 mmol) of lithium metal in 15 mL of freshly distilled ammonia. This solution was refluxed for 2 h and then quenched with ammonium chloride. Workup, as described earlier in the preparation of **6**, gave 180 mg of **9** as a solid having no carbonyl absorption in the infrared region.

Acid-Catalyzed Reaction of 9. A solution of 60 mg (0.15 mmol) of **9** in 4 mL of THF containing 4 drops of concentrated hydrochloric acid was stirred overnight at room temperature. The reaction mixture was diluted with ether, washed with sodium bicarbonate solution, and dried. Evaporation of the solvent yielded 55 mg of isomeric ketols, which were oxidized with Jones reagent. Chromatography of the crude oxidation product (silica gel) gave 47 mg (78%) of a mixture of **12** and **13** (70:30), together with trace amounts of **10** and **11**.

Base-Catalyzed Reaction of 14. To a solution of 10 mg (0.025 mmol) of **14** in 1 mL of THF at 0 °C was added 58 μL (0.075 mmol) of the previously described potassium hydroxide solution. After 2 h at 0 °C and then overnight at room temperature, the reaction mixture was diluted with either, washed with water, and dried. Evaporation of the solvent followed by chromatography of the residue gave 6 mg (60%) of **10** and 1 mg (10%) of **12** and **13** (70:30 mixture).

Base-Catalyzed Reaction of 9. To a solution of 60 mg (0.15 mmol) of **9** in 4 mL of THF was added 0.35 mL (0.45 mmol) of the previously used potassium hydroxide solution. This solution was stirred overnight, and the usual workup gave 52 mg of solid, which was then oxidized with Jones reagent. Chromatography of the crude product on silica gel gave 28 mg (46%) of **10** and 18 mg (30%) of a **12** and **13** mixture (70:30). A trace of **11** was also detected.

Reduction and Subsequent Base-Catalyzed Cleavage of 14. A solution of 4.0 mg (0.01 mmol) of **14** in 1 mL of THF was added to a solution of 4 mg (0.58 mmol) of lithium in 1 mL of freshly distilled ammonia. This solution was refluxed for 2 h and was then quenched with ammonium chloride. Workup gave 3 mg of a solid, which was dissolved in 1 mL of THF and treated with 29 μL (0.037 mmol) of potassium hydroxide solution. Following an overnight reaction period, this mixture was extracted with ether, and the resulting residue was oxidized by Jones reagent. Chromatography of the crude oxidation product on silica gel gave 2.0 mg (50%) of **10** as the only significant product.

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