isotopic analyses. Since the dextrorotatory acetate ester has been hydrolyzed under more drastic conditions than those employed to remove carbonyl bound O^{18}, without loss of optical activity,[3] it is unlikely that hydroxyl-bound O^{18} is affected. The analytically pure α-hydroxy ketone samples obtained by methods A and B contained 1.54 and 1.50 atom % excess of O^{18}, respectively

Within the limits of confidence of the isotopic analyses, the O^{18} distribution can be interpreted on the basis of a stereospecific, O–β-C, epoxy ether cleavage through IVc and/or its SN2 counterpart, in agreement with the Stevens mechanism. The intervention of other intermediates (*cf.* IVa, Va) would have resulted in a substantial loss of O^{18}. Thus, the anomalous α-C symmetrization, induced by the amino function, must occur during epoxy ether, (+)- or (−)-II, formation and following asymmetric induction of the ketone carbon.[3]

Experimental[9]

Labeling of (−)-I.—To 23.8 g. (0.1 moles) of (−)-I, prepared as previously described,[8] $[\alpha]^{25}D$ −3.6° (*c* 10.10, absolute ethanol), lit.[8] $[\alpha]^{27}D$ −4.2° (absolute ethanol), was added 110 ml. of 1 *N* hydrochloric acid. The solution was lyophilized and afforded a white crystalline material, m.p. 165.5–166.5°, $[\alpha]^{25}D < \pm 0.1°$ (*c* 10.00, water), $[\alpha]^{27}_{330}$ +90 ± 20° (*c* 0.0233, water), lit.[8b] $[\alpha]^{27}_{330}$ +130 (*c* 0.023, water). A small sample of the salt was used to regenerate the free amine, $[\alpha]^{25}D$ −3.8° (absolute ethanol).

A 21.9-g. (80-mmoles) sample of the hydrochloride salt was added to 20 ml. of O^{18}-enriched (5.85 atom % excess) water and warmed on a steam bath to effect complete solution. One drop of concentrated hydrochloric acid was added and heating (50°) was continued for 72 hr. The solution was lyophilized yielding a tan powder which was recrystallized from chloroform, m.p. 165–166°, afforded free amine, $[\alpha]^{25}D$ −3.6° (*c* 9.85, absolute ethanol), and contained 3.04 atom % excess of O^{18}.

Anal. Calcd. for $C_{13}H_{17}Cl_2NO$: C, 56.94; H, 6.25; Cl, 25.86. Found: C, 56.63; H, 6.48; Cl, 25.22.

(−)-2-Methoxy-2-phenyl-5-methyl-1-ox^{18}-5-azaspiro[2.5]octane [(−)-II].—Treatment of 5.58 g. (20 mmoles) of (−)-I hydrochloride with sodium methoxide in anhydrous methanol as described earlier[3] afforded 3.26 g. (14 mmoles, 70%) of (−)-II, b.p. 70–71° (0.08 mm.), containing 1.52 atom % excess of O^{18}: $[\alpha]^{26}D$ −1.3° (*c* 15.80, absolute ethanol).

Anal. Calcd. for $C_{14}H_{19}NO_2$: C, 72.07; H, 8.21; N, 6.00. Found: C, 71.90; H, 8.28; N, 6.25.

Acidolysis of (−)-2-Methoxy-2-phenyl-5-methyl-1-ox^{18}-5-azaspiro[2.5]octane [(−)-II].—Two 0.70-g. (3-mmoles) samples of (−)-II were treated according to methods A and B previously described.[3] However, in the case of cleavage with acetic acid (method B) the intermediate acetate ester was not isolated but was hydrolyzed directly. The reaction mixtures, after completion of the acidolysis and subsequent hydrolysis (method B), were made basic with sodium hydroxide and extracted with petroleum ether (b.p. 40–60°). The extract from each reaction mixture was re-extracted with 0.1 *N* hydrochloric acid. The acidic aqueous extract was heated (50–60°) in a water bath for 24 hr., made basic, and extracted with petroleum ether. After two additional cycles, the alcohols were recrystallized from the petroleum ether solution which had been dried over sodium sulfate, treated with charcoal, filtered through sintered glass, and concentrated. From reactions A and B there were obtained 0.550 g. (2.5 mmoles, 83%) and 0.631 g. (2.7 mmoles, 90%), respectively, of racemic α-hydroxy ketone, (±)-III, m.p. 56–57°, lit.[3] m.p. 56–57°, containing 1.54 and 1.50 atom % excess of O^{18}.

Anal. Calcd. for $C_{13}H_{17}NO_2$: C, 71.20; H, 7.81. Found (reaction A): C, 71.19; H, 7.61. Found (reaction B): C, 71.39; H, 7.86.

Acknowledgment.—We are indebted to Dr. H. Fales and Miss Katherine Warren of the National Institute of Health for the rotatory dispersion measurements.

(9) All melting points were obtained in a Hershberg [E. B. Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **8**, 312 (1936)] silicone (550-Dow) filled melting point apparatus equipped with Anschutz full-immersion thermometers. The samples were placed in the circulating silicone bath 10° below the reported melting points and heated at the rate of 1–2°/min. Elemental analyses were performed by Weiler and Strauss, Oxford, England. Isotopic (O^{18}) analyses were performed by Analytica Corp., New York, N. Y. Specific rotations were determined with a Zeiss 0.01° polarimeter in a modified [G. Hite and J. Lyons, *Chemist-Analyst*, **53**, 84 (1964)] 2-dm. (2-ml.) syringe-filling tube. The criterion for racemic products obtained from optically active starting materials was a level base line in the range 700–320 mμ as determined with a Rudolph manual spectropolarimeter. The O^{18}-enriched water was obtained from Isomet, Inc., Palisades Park, N. J.

A-Norsteroids. Ketalization of A-Nortestosterone

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The ketalization of Δ^4-3-keto steroids has been shown to give Δ^5-3-ketals,[1] Δ^4-3-ketals,[2] or mixtures of both[2] by varying conditions of acid strength or acid concentration. We wish to report our findings on the ketalization of a ring A steroidal α,β-unsaturated ketone in the A-nor series.[3]

The preparation of the ethylene ketal derivative of A-nortestosterone[4] (I) was carried out under reaction conditions (benzene, ethylene glycol, *p*-TsOH)[1,2] similar to those used for testosterone and 17β-hydroxy-A-nor-5α-androstan-2-one,[5] except that we found it necessary to conduct the reaction for a longer period of time (5–7 days) in order to obtain the ethylene ketal derivative (II) in reasonable yields. With varying concentrations of *p*-toluenesulfonic acid, however, only one ethylene ketal was obtained.

Evidence concerning the position of the double bond in II was obtained from the physical and chemical properties of the compound: (a) the change in optical rotation in going from the parent ketone to the ethylene ketal was dextrorotatory (−22° → +34°); this conversion is generally accompanied by a levorotatory shift in the formation of Δ^5-3-ketals[6]; (b) a relatively strong band appeared in the infrared spectrum at 6.03 μ; Δ^4-3-ethylene ketals are reported to absorb at 6.00 μ[2a,b]; and (c) when a solution of II in chloroform containing a trace of water was left overnight at room temperature, A-nortestosterone was obtained. The susceptibility of allylic ketals to mild acid hydrolysis has previously been noted.[2a,c]

(1) (a) E. F. Fernholz and H. E. Stavely, Abstracts, 102nd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1941, p. 39M; (b) R. Antonucci, S. Bernstein, R. Littel, K. J. Sax, and J. H. Williams, *J. Org. Chem.*, **17**, 1341 (1952); (c) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Am. Chem. Soc.*, **75**, 422 (1953).

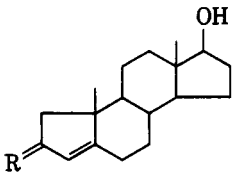
(2) (a) J. J. Brown, R. H. Lenhard, and S. Bernstein, *Experientia*, **18**, 310 (1962); *J. Am. Chem. Soc.*, **86**, 2183 (1964); (b) Q. R. Petersen and E. E. Sowers, *J. Org. Chem.*, **29**, 1627 (1964); (c) J. W. Dean and R. G. Christiansen, *ibid.*, **28**, 2110 (1963).

(3) J. Fried and E. Sabo [*J. Am. Chem. Soc.*, **84**, 4356 (1962)] have reported the ketalization of a Δ^5-3-keto-A-norsteroid with *p*-toluenesulfonic acid gives a mixture consisting mainly of the Δ^5-5β-3-ethylene ketal and a Δ^5-3-ethylene ketal.

(4) F. L. Weisenborn and H. E. Applegate, *ibid.*, **81**, 1960 (1959).

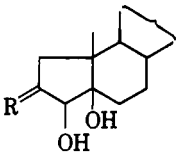
(5) R. Rull and G. Ourisson, *Bull. soc. chim. France*, 1573 (1958).

(6) L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, p. 309.



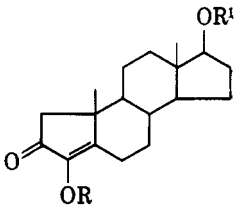
I, R = O

II, R = O—CH$_2$ / O—CH$_2$



III, R = O—CH$_2$ / O—CH$_2$

IV, R = O



V, R = R^1 = H

VI, R = R^1 = Ac

VII, R = CH$_3$; R^1 = H

These data indicated that the double bond in II was in ring A. Confirmation for this conclusion was obtained in the following manner. Treatment of II with osmium tetroxide and decomposition of the resulting osmate ester with an alkaline mannitol solution[7] afforded a single diol (n.m.r., t.l.c.) III which on acid hydrolysis gave a ketotriol IV, whose n.m.r. spectrum showed signals for the protons on the carbons bearing the secondary alcohols at τ 5.55 and 6.35. The multiplet at τ 6.35 could be assigned to the C-17 hydrogen and since the peak at 5.55 was a singlet it was assigned to the C-3 hydrogen. If the hydroxyl were at C-6, the n.m.r. signal should be split by the hydrogens at C-7.

Further, dehydration of the ketotriol in ethanolic potassium hydroxide solution gave a product (V) which exhibited ultraviolet absorption characteristic of a diosphenol (λ_{max}^{EtOH} 265 mμ, λ_{max}^{NaOH} 303 mμ with a lower extinction coefficient). This evidence placed the *cis*-glycol at C-3, C-5 and left the configuration at these centers to be established.

Direct evidence for the 3β,5β-diol (IV) configuration was obtained from the optical rotatory dispersion (O.R.D.) curve. The O.R.D. curve of IV should be that of a 5β-(H)-2-keto-A-norsteroid since usually neither angular substitution (hydroxyl for hydrogen) at a position nonadjacent to a ketone, nor introduction of a hydroxyl function adjacent to the ketone affects the sign of the O.R.D. curve.[8] Indeed, the O.R.D. curve of IV exhibited a negative Cotton effect ([α]$_{321}$ $-1893°$, minimum) similar in both sign and amplitude to methyl 2-keto-A-norcholanate[9] ([α]$_{312.5}$ $-1900°$, minimum).

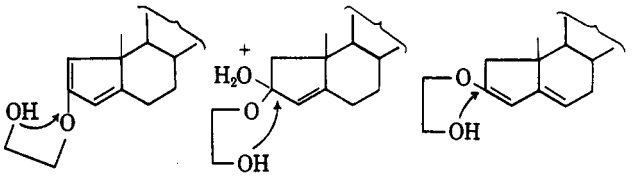
The osmium tetroxide hydroxylation of cholestenone yields a mixture of the 4α,5α-diol and the 4β,5β-diol.[10] The reaction of A-nortestosterone with osmium tetroxide was investigated with the hope of being able to isolate an isomeric diol. Decomposition of the intermediate osmate ester with an alkaline mannitol solution or biphasic treatment[11] of the osmate ester in benzene–methanol with sodium sulfite and potassium carbonate resulted in dehydration to the diosphenol V,[12] and decomposition of the osmate ester with hydrogen sulfide[13] led to a single 3,5-diol in 60% yield identical with IV.

From an inspection of models of I and II attack by the bulky osmic acid would seem to be favored from the β-side. Attack from the α-side is somewhat more hindered by the interference of the axial hydrogens at C-7 and C-9 and ring A which is folded toward ring B on the α-side.

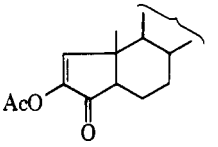
Acetylation of V afforded the diacetate VI,[14] while treatment of V with methanol in the presence of boron trifluoride[15] gave 3-methoxy-A-nortestosterone (VII).

Since testosterone has been demonstrated to yield either the Δ^5-3-ketal or a mixture of the Δ^4- and Δ^5-3-ketals under similar reaction conditions,[1b,2c] the exclusive formation of the Δ^3-2-ketal in the case of A-nortestosterone merits discussion. In the normal steroid series a $\Delta^{3,5}$-dienol ether which undergoes 1,2-addition of the primary hydroxyl to the 3,4 double bond has been proposed as the intermediate in the formation of the Δ^5-3-ketal,[16] whereas 1,2-addition to a $\Delta^{2,4}$-dienol ether or displacement of water from its precursor would lead to the Δ^4-3-ketal.[2a,c]

The isolation of II as the sole product requires that either VIII or IX be the intermediate in its formation. The failure to obtain any of the Δ^5-2-ketal may be attributed to the fact that the $\Delta^{2,5}$-dienol ether X does not form easily in A-norsteroids. In fact, the $\Delta^{2,5}$-dienol acetate of A-norcholestenone has not been isolated even under forcing conditions.[17,18]



VIII IX X



XI

(7) R. Criegee, B. Marchand, and H. Wannowius, *Ann.*, **550**, 99 (1942).

(8) C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., Inc., New York, N. Y., 1960.

(9) C. Djerassi, R. Riniker, and B. Riniker, *J. Am. Chem. Soc.*, **78**, 6362 (1956).

(10) J. Eastham, G. B. Miles, and C. A. Krauth, *ibid.*, **81**, 3114 (1959).

(11) W. S. Allen and S. Bernstein, *ibid.*, **78**, 1909 (1956).

(12) E. Caspi, W. Schmid, and B. T. Khan [*J. Org. Chem.*, **26**, 3898 (1961)] reported that reaction of adrenosterone with osmium tetroxide afforded the osmate ester in good yield, but that cleavage of the ester with an alkaline mannitol solution proved difficult and the yield of glycol was not satisfactory. A likely possibility, however, is that cleavage proceeded readily to a mixture of stereoisomeric *cis*-glycols, the major portion of which underwent dehydration to 4-hydroxyandrenosterone.

(13) D. H. R. Barton and D. Elad, *J. Chem. Soc.*, 2085 (1956).

(14) The alternate structure XI is excluded by the absence of a vinyl proton peak in the n.m.r. spectrum (see Experimental).

(15) R. Stevenson and L. F. Fieser, *J. Am. Chem. Soc.*, **78**, 1409 (1956).

(16) C. Djerassi and M. Gorman, *ibid.*, **75**, 3704 (1954).

(17) T. L. Jacobs and N. Takahashi, *ibid.*, **80**, 4865 (1958).

(18) W. G. Dauben and G. A. Boswell [*ibid.*, **83**, 5003 (1961)] obtained an oily product whose ultraviolet spectrum showed the presence of the $\Delta^{2,5}$-dienol acetate contaminated with starting material.

Experimental

Melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. Values of $[\alpha]_D$ have been approximated to the nearest degree and were taken in 95% ethanol. Ultraviolet spectra were determined in 95% ethanol, infrared spectra in pressed potassium bromide pellets, and n.m.r. spectra in deuteriochloroform with tetramethylsilane as internal standard. All evaporations were carried out *in vacuo*.

2-Ethylenedioxy-17β-hydroxy-A-norandrost-3-en-2-one (II). A.—A mixture of A-nortestosterone (I, 4 g.), *p*-toluenesulfonic acid monohydrate (165 mg.), benzene (250 ml.), and ethylene glycol (40 ml.) was stirred and refluxed for 7 days. The water formed during the reaction was removed by a Dean–Stark moisture trap fitted with a calcium carbide thimble. The reaction mixture was treated with pyridine (1 ml.), the benzene layer was separated, and the ethylene glycol layer was diluted with water and extracted with additional benzene. The combined benzene extracts were washed with 8% salt solution, dried over sodium sulfate, and evaporated. The residue was crystallized from isopropyl ether to yield II (2.45 g.): m.p. 149.5–150.5°; $[\alpha]^{29}_D$ +34° (*c* 1.13); λ 2.88 (OH) and 6.03 μ (C=C); τ 9.22 (s, 18-Me), 8.96 (s, 19-Me), 6.32 (m, 17-H), 6.05 (s, ketal methylenes), and 4.73 (d, J = 1–2 c.p.s., 3-H).

Anal. Calcd. for $C_{20}H_{30}O_3$ (318.44): C, 75.43; H, 9.50. Found: C, 75.52; H, 9.47.

Recrystallization of the residue obtained by evaporation of the mother liquor from isopropyl ether gave additional II (616 mg., m.p. 146–147°). Plate chromatography of the residue using Woelm neutral alumina (activity V) as adsorbent and chloroform as the developing solvent gave a major band at R_f 0.5, which was detectable by iodine vapor and which on elution with ethyl acetate gave a residue which upon crystallization from isopropyl ether afforded additional II (113 mg., m.p. 145.5–146.5°; 152 mg., m.p. 143–145°).

B.—A-Nortestosterone (1 g.) was ketalized as described above in benzene (150 ml.) with ethylene glycol (30 ml.) and *p*-toluenesulfonic acid monohydrate (15 mg.) to give a 55% yield of II.

2-Ethylenedioxy-3β,5β,17β-trihydroxy-A-norandrostan-2-one (III).—A mixture of II (50 mg.) and osmium tetroxide (47 mg.) in pyridine (0.4 ml.) and benzene (10 ml.) was stirred at room temperature for 89 hr. The reaction mixture was evaporated and the residue was dissolved in chloroform (8 ml.) and stirred with a 1% potassium hydroxide solution (16 ml.) containing mannitol (1.6 g.) for 3 hr. The chloroform layer was separated and dried over sodium sulfate. Evaporation gave III (54 mg., m.p. 204–207°). Recrystallization from benzene gave the analytical sample: m.p. 208–209°; $[\alpha]^{22}_D$ +46° (*c* 0.19); λ 2.90 (OH) and 3.00 μ (OH); τ 9.25 (s, 18-Me), 9.01 (s, 19-Me), 6.37 (m, 17-H), and 6.04 (s, ketal methylenes).

Anal. Calcd. for $C_{20}H_{32}O_5$ (352.46): C, 68.15; H, 9.15. Found: C, 68.19; H, 9.13.

3β,5β,17β-Trihydroxy-A-norandrostan-2-one (IV). A.—A mixture of III (225 mg.) and *p*-toluenesulfonic acid monohydrate (17 mg.) in water (2 ml.) and acetone (8 ml.) was refluxed for 5 hr. The reaction mixture was evaporated, diluted with water, and extracted three times with ethyl acetate. The ethyl acetate extracts were washed with a saturated sodium bicarbonate solution and 8% salt solution, dried over sodium sulfate, and evaporated. The residue was crystallized from ethyl acetate to afford IV (56 mg., m.p. 202–204°). Recrystallization from ethyl acetate gave the analytical sample: m.p. 206–207°; $[\alpha]^{22}_D$ −40° (*c* 0.62); λ 2.86 (OH), 2.93 (OH), and 5.75 μ (2-one); τ 9.20 (s, 18-Me), 8.85 (s, 19-Me), 6.35 (m, 17-H), and 5.55 (s, 3-H); O.R.D.[19] (*c* 0.06, methanol), $[\alpha]_{550}$ −40°, $[\alpha]_{321}$ −1893°, and $[\alpha]_{290}$ +1666°.

Anal. Calcd. for $C_{18}H_{28}O_4$ (308.42): C, 70.10; H, 9.15. Found: C, 70.20; H, 9.11.

B.—A mixture of I (3.25 g.) and osmium tetroxide (3.0 g.) in pyridine (3 ml.) and benzene (60 ml.) was stirred at room temperature for 2 days. The reaction mixture was diluted with dioxane (100 ml.) and hydrogen sulfide was bubbled through the solution for 5 min. The precipitate was removed by filtration through Celite,[20] the filtrate was evaporated, and the residue was crystallized from ethyl acetate to give IV (1.17 g., m.p. 203–205°). Recrystallization of the residue obtained by evaporation of the mother liquor from ethyl acetate–hexane gave additional IV (581 mg., m.p. 197–199°; 323 mg., m.p. 198–200°).

3,17β-Dihydroxy-A-norandrost-3-en-2-one (V). A.—A mixture of I (1.18 g.) and osmium tetroxide (1.1 g.) in pyridine (1 ml.) and benzene (20 ml.) was stirred at room temperature for 65.5 hr. The reaction mixture was evaporated and the residue was dissolved in chloroform (100 ml.) and stirred with a 1% potassium hydroxide solution (200 ml.) containing mannitol (20 g.) for 2.5 hr. The layers were separated and the aqueous phase was acidified with hydrochloric acid and extracted five times with chloroform. The chloroform extracts were dried over sodium sulfate and evaporated. Crystallization of the residue from acetone–hexane gave V (292 mg., m.p. 254.5–255.5°). The analytical sample was prepared by recrystallization from acetone–hexane and had m.p. 259–260°: $[\alpha]^{29}_D$ +65° (*c* 0.48); λ 2.93 (17-OH), 3.18 (3-OH), 5.87 (2-one), and 6.02 μ (C=C); τ 9.19 (s, 18-Me), 8.83 (s, 19-Me), 6.33 (m, 17-H), and 4.63 (s, 3-OH); λ 265 mμ (ε 12,700); λ^{NaOH} 303 mμ (ε 9800).

Anal. Calcd. for $C_{18}H_{26}O_3$ (290.39): C, 74.44; H, 9.03. Found: C, 74.31; H, 9.01.

B.—A solution of IV (24 mg.) in chloroform (5 ml.) was stirred with a 1% potassium hydroxide solution (10 ml.) containing mannitol (1 g.) for 3 hr. and worked up as described above to give V (5 mg., m.p. 259.5–260.5°).

C.—A mixture of I (920 mg.) and osmium tetroxide (853 mg.) in pyridine (1 ml.) and benzene (25 ml.) was stirred at room temperature for 3 days. The reaction mixture was diluted with benzene (25 ml.) and treated with potassium bicarbonate (3.6 g.) and sodium sulfite (3.6 g.) in water (45 ml.). Methanol (25 ml.) was added and the reaction mixture was stirred at room temperature for 1 day. The reaction mixture was filtered, and the layers were separated. The benzene layer was dried over sodium sulfate and evaporated. The residue was crystallized from ethyl acetate to give V (192 mg., m.p. 259–260°). Recrystallization of the residue obtained by evaporation of the mother liquor gave additional V (96 mg., m.p. 257–258°; 27 mg., m.p. 256–257°).

3,17β-Diacetoxy-A-norandrost-3-en-2-one (VI).—A mixture of V (275 mg.), pyridine (0.4 ml.), and acetic anhydride (2 ml.) was allowed to stand at room temperature for 65 hr. The reaction mixture was poured onto ice and extracted three times with ether. The ether extracts were washed with a saturated sodium bicarbonate solution and 8% salt solution, dried over sodium sulfate, and evaporated. The residue was crystallized from isopropyl ether to give VI (139 mg., m.p. 182–184°). Recrystallization from isopropyl ether gave the analytical sample: m.p. 188.5–189.5°; $[\alpha]^{22}_D$ −3° (*c* 0.22); λ 5.66 (3-acetate), 5.83 (17-acetate and 2-one), and 6.01 μ (C=C); τ 8.98 (s, 18-Me), 8.78 (s, 19-Me), 7.96 (s, 17-acetate), 7.75 (s, 3-acetate), and 5.40 (m, 17-H); λ 240 mμ (ε 15,000).

Anal. Calcd. for $C_{22}H_{30}O_5$ (374.46): C, 70.56; H, 8.08. Found: C, 70.38; H, 7.91.

3-Methoxy-17β-hydroxy-A-norandrost-3-en-2-one (VII).—A solution of V (96 mg.) in methanol (20 ml.) containing boron fluoride etherate (0.1 ml., freshly distilled) was refluxed for 18 hr. The reaction mixture was evaporated, diluted with water, and extracted three times with ethyl acetate. The ethyl acetate extracts were washed with 8% salt solution, dried over sodium sulfate, and evaporated. The residue was crystallized from ether to afford VII (41 mg., m.p. 129–130°; 22 mg., m.p. 127.5–128.5°). Recrystallization from isopropyl ether gave the analytical sample: m.p. 129–130°; $[\alpha]^{29}_D$ +55° (*c* 0.71); λ 2.88 (OH), 5.88 (2-one), and 6.06 μ (C=C); τ 9.20 (s, 18-Me), 8.85 (s, 19-Me), 6.34 (m, 17-H), and 6.15 (s, 3-OCH_3); λ 253 mμ (ε 11,300) and 306 mμ (ε 336).

Anal. Calcd. for $C_{19}H_{28}O_3$ (304.41): C, 74.96; H, 9.27. Found: C, 75.04; H, 9.28.

Acknowledgment.—The authors wish to thank the following members of the Squibb Institute for their contributions to this work: Dr. A. Cohen for the n.m.r. spectra, Mr. J. Alicino and Mr. C. Sabo for the microanalyses, Miss B. Keeler and Miss R. Karitzky for the infrared spectra, and Mr. W. Bullock for the ultraviolet spectra.

(19) The O.R.D. curve was determined by Professor A. K. Bose, Stevens Institute of Technology.

(20) Celite is Johns-Manville's trade-mark for diatomaceous silica products.