drazones resulted in dark reaction mixtures from which no isolable products were obtained.

A reasonable assumption to explain the course of the successful reactions is initial formation of a quaternary intermediate (I) followed by scission at the N–N bond. The higher rate in the more polar solvent tends to support this view. In expt 5 and 6 the reactions were exothermic with maximum yields not obtained until 24 hr. Presumably the intermediates in these reactions have a lower ground state energy and greater stability. However, all attempts to isolate the postulated quaternary intermediate were unsuccessful.

A mechanism similar to that proposed by Smith and Walker[2] in which the solvent assumes the role of the base may be operating.

Experimental Section[3]

Preparation of Hydrazones.—Hydrazones were prepared in the usual manner by allowing equimolar amounts of the unsymmetrical dialkylhydrazine to react with an aldehyde or ketone in a benzene solution. The formed water was removed and the product distilled *in vacuo*. The products are described in Table II. Compounds **2**, **3**, and **5** have not been previously reported in the literature.

4-Bromophenacyltrimethylhydrazinium Bromide.—To 20.0 g (0.072 mole) of 2,4′-dibromoacetophenone in 190 ml of dry acetonitrile was added 4.4 g (0.073 mole) of N,N-dimethylhydrazine. After 1 hr the colorless solid was filtered and dried *in vacuo* to yield 24.0 g, mp 141–143° dec (99%). The analysis was performed on the crude material since recrystallization and heat resulted in partial decomposition.

Anal. Calcd for $C_{10}H_{14}Br_2N_2O$: C, 35.53; H, 4.17; Br, 47.28; N, 8.29. Found: C, 35.66; H, 4.44; Br, 47.43; N, 8.31.

Reaction of Benzaldehyde Dimethylhydrazone with 2,4′-Dibromoacetophenone.—To a slurry of 18.6 g (0.0675 mole) of 2,4′-dibromoacetophenone in 100 ml of acetonitrile was added 10.0 g (0.0675 mole) of benzaldehyde dimethylhydrazone. The mixture was stirred for 15 min during which the solution became homogeneous and a solid had precipitated. The mixture was allowed to stand for 24 hr and filtered; the precipitate was washed with ether to yield 20.8 g of 2-dimethylamino-4′-bromoacetophenone, mp 190–192°.

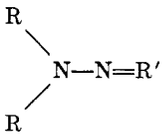
Anal. Calcd for $C_{10}H_{13}Br_2N_2O$: C, 37.18; H, 4.05; Br, 49.53; N, 4.34. Found: C, 37.48; H, 3.99; Br, 49.28; N, 4.28.

The filtrate was evaporated *in vacuo* to yield 6.0 g of a brown liquid which was distilled to yield 4.9 g (71%) of benzonitrile of boiling point 190°. The infrared spectra and refractive index were identical with those of an authentic sample of benzonitrile.

N-Benzyl-N,N-dimethyl-N′-butylidene Hydrazonium Bromide.—To a solution of 6.7 g (0.0584 mole) of butyraldehyde dimethylhydrazone in 40 ml of acetonitrile was added 10.0 g (0.0584 mole) of benzyl bromide. After 16 hr the solvent was removed *in vacuo* and the colorless solid residue was recrystallized from benzene–hexane to give 13 g (78%). Recrystallization from benzene gave a product with a melting point of 82–86° dec.

Anal. Calcd for $C_{13}H_{21}BrN_2$: C, 54.73; H, 7.42; N, 9.82. Found: C, 54.33; H, 7.58; N, 9.40.

TABLE II
HYDRAZONES



No.	R	R	R′	Mp or bp, °C (mm)	$n^{20}D$
1	CH_3	CH_3	CHC_3H_7	134 (760)[a]	1.4420
2	$(CH_2)_5$		CHC_3H_7	70–74 (8)[b]	1.4791
3	CH_3	CH_3	CHC_6H_{11}	124–128 (50)[c]	1.4821
4	CH_3	CH_3	CHC_6H_5	144–146 (35)[d]	1.5988
5	CH_3	CH_3	$CH(o\text{-}NO_2C_6H_4)$	104–105 (0·04)[e]	
6	CH_3	CH_3	$CH(p\text{-}NO_2C_6H_4)$	110–112[f]	
7	CH_3	CH_3	C_6H_{10}[g]	62–64 (10)[h]	1.4740

[a] Lit. bp 136–140°, $n^{24}D$ 1.4390. R. H. Wiley, S. C. Slaymaker, and H. Kraus, *J. Org. Chem.*, **22**, 204 (1957). [b] Picrate, mp 103–104°. *Anal.* Calcd for $C_9H_{18}N_2$ (base): C, 70.07; H, 11.76; N, 18.16. Found: C, 70.23; H, 11.40; N, 17.88. [c] Picrate, mp 156–158°. *Anal.* Calcd for $C_{15}H_{21}N_5O_7$ (picrate): C, 46.99; H, 5.52; N, 18.27. Found: C, 47.27; H, 5.76; N, 18.28. [d] Lit. bp 127–128° (20 mm), $n^{29}D$ 1.5920. D. Todd, *J. Am. Chem. Soc.*, **71**, 1353 (1949). [e] *Anal.* Calcd for $C_9H_{11}N_3O_2$: C, 55.95; H, 5.74; N, 21.75. Found: C, 56.22; H, 5.85; N, 21.81. [f] Lit. mp 111°. O. L. Brady and G. P. McHugh, *J. Chem. Soc.*, **121**, 1651 (1922). [g] Cyclohexylidene. [h] Lit. bp 177–180°, $n^{27}D$ 1.4697. See footnote *d*.

(3) Melting points were determined on a calibrated Fisher-Johns apparatus. Elemental analysis were performed by Midwest Microlab, Inc., Indianapolis, Ind. 46226.

Alkaline Hydrogen Peroxide Oxidation of a Steroidal α,β-Unsaturated Ketone. A Baeyer–Villiger Product[1]

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Received April 5, 1966

The alkaline hydrogen peroxide oxidation of A-nortestosterone gives rise to a mixture of products which includes the epoxy lactone, 2-oxa-4β,5β-oxido-17β-hydroxyandrostan-3-one. The structure, stereochemistry, and mode of formation of this Baeyer–Villiger product are discussed.

The oxidation of α,β-unsaturated ketones with alkaline hydrogen peroxide has been observed to lead to the exclusive formation of epoxy ketones (**1**), without any evidence of Baeyer–Villiger products.[2] This is in sharp contrast to the oxidation of Δ^4-3-keto steroids with various peracids, in which an enol lactone (**2**) has been isolated[3] or postulated[4–6] as the initial Baeyer–Villiger product. A similar enol lactone has also been suggested as an intermediate in the oxidation of a Δ^4-3-keto steroid with hydrogen peroxide in the presence of catalytic amounts of selenium dioxide[7] (Scheme I). During the course of the alkaline hydrogen peroxide

(1) A preliminary account of this material has appeared: S. D. Levine, *Tetrahedron Letters*, 2233 (1965).

(2) C. H. Hassall, *Org. Reactions*, **9**, 73 (1957).

(3) E. Caspi, Y. M. Chang, and R. I. Dorfman, *J. Med. Pharm. Chem.*, **5**, 714 (1962).

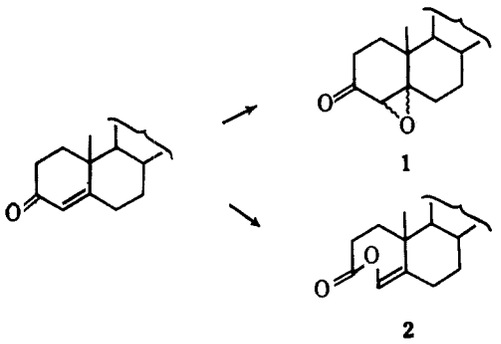
(4) G. Pettit and T. Kasturi, *J. Org. Chem.*, **26**, 4557 (1961).

(5) A. Salamon, *Z. Physiol. Chem.*, **272**, 71 (1941).

(6) J. T. Pinhey and K. Schaffner, *Tetrahedron Letters*, 601 (1965).

(7) E. Caspi and S. N. Balasubrahmanyam, *Experientia*, **19**, 396 (1963).

SCHEME I



oxidation of an A-nor steroid, a novel oxidation product was isolated and is the subject of this discussion.

A-Nortestosterone[8] (**3**) (Chart I) was treated overnight at room temperature with 30% hydrogen peroxide and 4 *N* sodium hydroxide in methanol and the crude reaction product refluxed in glacial acetic acid saturated with hydrogen chloride. Chromatography of the product on neutral alumina afforded a chlorine-containing compound (+ Beilstein) in low yield (5%). The infrared spectrum exhibited major peaks at λ 5.80, 6.22, and 8.15 μ which seemed in agreement with those anticipated for the expected product, 3-chloro-A-nortestosterone acetate (**4**). However, the microanalysis indicated the presence of an additional oxygen atom in the molecule. This compound was formulated as the 2-oxa-4-chloro-4-dehydro steroid (**5**) on the basis of the following evidence: (a) two protons appeared in the nmr spectrum as an AB quartet, τ 5.77 and 5.97, J = 11 cps, consistent with a methylene group situated between an oxygen atom and an angular carbon atom bearing a methyl group; and (b) the ultraviolet spectrum exhibited a peak at λ 239 mμ (ε 11,200). This represents a bathochromic shift of 15.5 mμ compared with the ultraviolet absorption maximum of the unsubstituted lactone (2-oxaandrost-4-en-3-one-17β-ol[9]) and is comparable with the predicted increment for an α-chloro group in a conjugated enone system.[10]

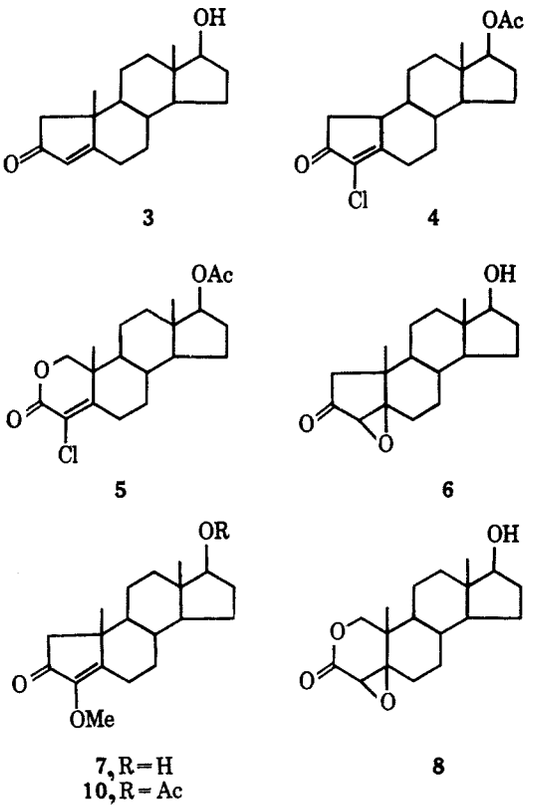
A logical precursor of **5** would be an epoxy lactone which opened on treatment with the hydrogen chloride in acetic acid. In order to gain insight into the actual nature of the intermediate(s) leading to the formation of **5**, the oxidation of **3** was repeated and the crude product separated into a neutral and a base-soluble fraction.

Chromatography of the neutral fraction first on alumina and then on silica gel afforded two components. One of the compounds analyzed as $C_{18}H_{26}O_3$, which indicated the introduction of an additional oxygen atom into the molecule. This substance was formulated as the expected product of the epoxidation reaction, 3β,5β-oxido-A-norandrostan-2-one-17β-ol (**6**). In accord with this structure two multiplets appeared in the nmr spectrum at τ 6.39 and 6.87. The former could be assigned to the 17α proton and the latter to the 3α proton. The assignment of the β orientation to the epoxide is based on analogy to the preferred β-side addition to the Δ^3-2-one system in A-nor steroids. For example, osmium tetroxide hydroxylation of **3** affords the 3β,5β-diol,[11] cyanation of **3** affords 5β-cyano-A-nordihydrotestosterone,[12] and catalytic hydrogenation of **3** gives the 5β-dihydro derivative.[8] Further evidence for the β orientation of the epoxide will be presented later.

The more polar component of the neutral fraction was characterized as 3-methoxy-A-nortestosterone (**7**) by a comparison of its melting point and infrared, and nmr spectra with those of an authentic sample.[11]

Acidification of the base-soluble fraction and chromatography on alumina afforded as anticipated, an epoxy lactone in 15% yield. A poorly resolved quartet centered at τ 6.00 appeared in the nmr spectrum for the C-1 methylene group. It was formulated as the 4β,5β-oxidolactone (**8**) and its stereochemistry will be discussed shortly. This represents the first example of a Baeyer–Villiger product from an α,β-unsaturated ketone under these reaction conditions and provides a new route to 2-oxa steroids.[13] Treatment of **8** with glacial acetic acid saturated with hydrogen chloride afforded the chloro lactone **5**.

CHART I



3 **4** **5** **6** **7**, R = H; **10**, R = Ac **8**

In view of these findings, the formation of the 2-oxa steroid may be envisioned as proceeding in the following manner. Initial epoxidation of **3** leads to **6**, which reacts either with the methanol to give **7** or is oxidized further by the hydrogen peroxide to the Baeyer–Villiger product **8** (Scheme II).

If this indeed represents the reaction pathway, then it follows that the orientation of the epoxide moiety

(8) F. L. Weisenborn and H. E. Applegate, *J. Am. Chem. Soc.*, **81**, 1960 (1959).

(9) R. Pappo and C. J. Jung, *Tetrahedron Letters*, 365 (1962).

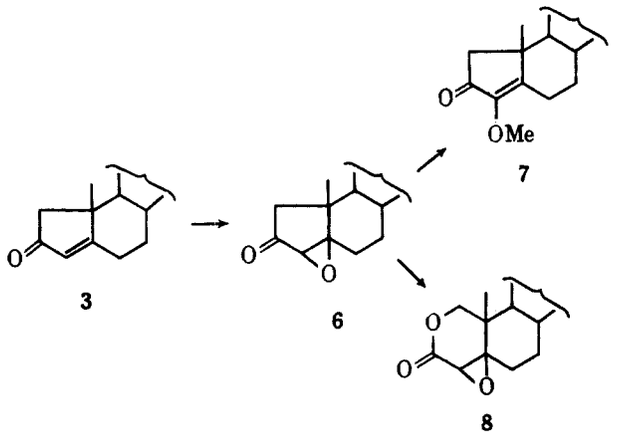
(10) L. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959, p 19.

(11) S. D. Levine and P. A. Diassi, *J. Org. Chem.*, **30**, 1325 (1965).

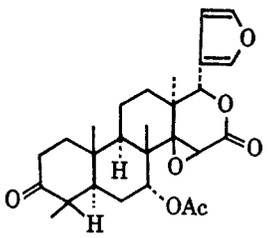
(12) S. D. Levine, *Steroids*, 477 (1966).

(13) During the course of this investigation, the conversion of 2-oxo-A-nor steroids in both the 5α and 5β series *via* perbenzoic acid oxidation to 2-oxa steroids has been reported: S. Hara, *Chem. Pharm. Bull.*, **12**, 1531 (1964).

SCHEME II



in both **6** and **8** must be identical, since the insertion of the oxygen atom into ring A *via* the Baeyer–Villiger reaction would not alter the stereochemistry of the epoxide. The epoxide group in **6** was assigned the β configuration on the basis of chemical analogy (*vide supra*); therefore the epoxide in **8** should be β oriented. Direct evidence for the β-epoxide stereochemistry in **8** was obtained from its circular dichroism (CD) curve. The CD curve of **8** exhibited a positive maximum at about 235 mμ ($\Delta\epsilon \sim +6$), which is in excellent agreement with the negative minimum observed in the CD curve[14] of dihydrogedunin (**9**)[15] at 238 mμ ($\Delta\epsilon \sim -4$). At this stage there still exists the possibility that **6** is actually an α-epoxide and that the β-epoxide was completely converted to **7** or **8** and/or was not even isolated from the reaction mixture. Definite proof that **6** is actually the β-epoxide was obtained by treating it with alkaline hydrogen peroxide and converting it to **8** (infrared, nmr, melting point, mixture melting point).



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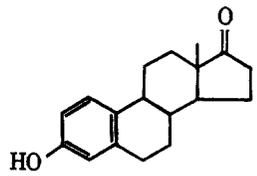
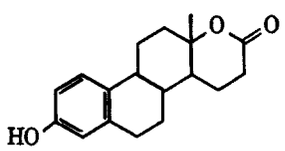
In addition, it also appeared obvious that by utilizing a solvent which would not be expected to react with the initially formed epoxide **6**, an increased yield of **8** should be realized. When the reaction was conducted in dioxane, the oxidation proceeded slowly and the crude reaction product contained a considerable amount of unreacted **3**. However, when *t*-butyl alcohol was employed as the solvent and the reaction time was extended to 6 days, a 40% yield of the 2-oxa steroid **8** was obtained.

In another experiment, **3** was oxidized as previously in methanol and the crude reaction product was treated in chloroform and ethanol with hydrogen chloride. Chromatography on Florisil afforded a 1:2 mixture of 3-chloro- and 3-methoxy-A-nortestosterone as evidenced by nmr. These two substances could be separated after acetylation by chromatography on silica gel. The less polar compound was identified as 3-chloro-A-nortestosterone acetate (**4**). The chloro compound exhibited a maximum at 246 mμ in the ultraviolet and major bands in the infrared spectrum at 5.80, 6.13, and 8.04 μ. The 3-methoxy derivative **10** exhibited a maximum at 250 mμ in the ultraviolet and a signal at τ 6.13 for the OCH_3 group in the nmr spectrum.

In retrospect, it is not altogether surprising, that the first example of a Baeyer–Villiger product from the alkaline hydrogen peroxide oxidation of an α,β-unsaturated ketone should be observed with a cyclopentenone system. Over 20 years ago, Westerfeld oxidized estrone (**11**) with 10% hydrogen peroxide and 1 *N* sodium hydroxide for 3 days and isolated the 17a-oxa-17-one (**12**) in 20% yield.[16] The oxidation of





cyclopentanone under these same conditions led to the formation of δ-valerolactone in a similar manner. In the example presented herein, the initial oxidation leads to a ring A substituted cyclopentanone (**6**) which is then further oxidized to a δ-lactone (**8**).

Experimental Section[17]

2-Oxa-4-chloro-17β-acetoxyandrost-4-en-3-one (5). A.—A solution of A-nortestosterone (**3**, 1 g) in methanol (10 ml) was cooled to 5° and treated with 30% hydrogen peroxide (4 ml) and 4 *N* sodium hydroxide (2 ml), and stirred at room temperature for 17.5 hr. The reaction mixture was diluted with water and acidified and the precipitate was collected by filtration (526 mg). The filtrate was extracted with chloroform; the chloroform extracts were washed with 8% salt solution, dried, and evaporated to give 497 mg of an oil, which was combined with the precipitate. The crude reaction product was refluxed for 16.5 hr in glacial acetic acid (25 ml) saturated with hydrogen chloride. The reaction mixture was evaporated and the residue was taken up in chloroform. The chloroform solution was washed with a saturated sodium bicarbonate solution, 8% salt solution, dried, and evaporated. Plate chromatography of the residue on alumina using chloroform–1% methyl alcohol as the developing solvent gave a major band which was detectable by iodine vapor. Elution with ethyl acetate and crystallization of the residue from isopropyl ether gave **5** (67 mg, mp 203–206°). Recrystallization from isopropyl ether–acetone gave the analytical sample: mp 238.5–240.5°; $[\alpha]^{23}D$ +45°; λ 5.80 (lactone and acetate), 6.22 (C=C), and 8.15 μ (acetate); λ 239 mμ (ϵ 11,200); τ

(14) Personal communication from Professor G. Snatzke (University of Bonn). The author thanks Professor Snatzke for determining the CD curve of **8** and for his valuable comments. If one examines models of **8** and **9**, it is apparent that the angle between the carbonyl and the epoxide ring is smaller in **8** than in **9** and therefore the interaction should be greater in **8**. This is in agreement with the greater ellipticity observed for **8** in the CD curve.

(15) (a) A. A. Kisanya, C. W. L. Bevan, T. G. Halsall, J. W. Powell, and D. A. H. Taylor, *J. Chem. Soc.*, 3705 (1961); (b) S. A. Sutherland, G. A. Sim, and J. M. Robertson, *Proc. Chem. Soc.*, 222 (1962).

(16) W. Westerfeld, *J. Biol. Chem.*, **143**, 177 (1942).

(17) Melting points were taken on a Fisher-Johns melting point apparatus and are uncorrected. Optical rotations were determined in chloroform on a Perkin-Elmer 141 polarimeter and the values of $[\alpha]D$ have been approximated to the nearest degree. Infrared spectra were determined on a Perkin-Elmer 21 spectrometer in pressed potassium bromide pellets, ultraviolet spectra on a Cary 11 spectrometer in ethyl alcohol, and nmr spectra on a Varian A-60 in deuteriochloroform with tetramethylsilane as internal standard. The alumina used for chromatography refers to Merck, A. G. neutral alumina (activity V), and the silica gel to Davison 100–200 mesh. Solutions were dried over sodium sulfate and all evaporations were carried out *in vacuo*.

9.16 (s, 18-Me), 8.74 (s, 19-Me), 7.96 (s, 17-acetate), 5.97 and 5.77 (q, J = 11 cps, 2-CH_2) and 5.39 (m, 17-H).

Anal. Calcd for $C_{20}H_{27}ClO_4$ (366.87): C, 65.47; H, 7.42; Cl, 9.66. Found: C, 65.87; H, 7.80; Cl, 9.62.

B.—A solution of **8** (158 mg) in glacial acetic acid (10 ml) saturated with hydrogen chloride was refluxed for 16 hr and processed as described above to give **5** (30 mg, mp 212–214°). Recrystallization from isopropyl ether–acetone gave material melting at 238.5–240.5°.

3β,5β-Oxido-17β-hydroxy-A-norandrostane-2-one (6) and 3-Methoxy-17β-hydroxy-A-norandrost-3-en-2-one (7).[11]—A solution of A-nortestosterone (3, 2 g) in methyl alcohol (20 ml) at 5° was treated with 30% hydrogen peroxide (8 ml) and 4 N sodium hydroxide (4 ml) and stirred at room temperature for 16 hr. The reaction mixture was diluted with water and extracted with ether. The ether extracts were washed with 8% salt solution, dried, and evaporated. Plate chromatography of the residue (835 mg) on alumina using chloroform–2% methyl alcohol as the developing solvent gave five bands which were detectable by iodine vapor. Elution of band 3 with ethyl acetate and crystallization of the residue from isopropyl ether gave **6** (35 mg, mp 142–144°). Recrystallization from isopropyl ether gave the analytical sample: mp 144–145°; $[\alpha]^{26}D$ +102°; λ 2.83 (OH) and 5.77 μ (2-one); τ 9.22 (s, 18-Me), 8.82 (s, 19-Me), 6.87 (m, 3-H) and 6.39 (m, 17-H).

Anal. Calcd for $C_{18}H_{26}O_3$ (290.39): C, 74.44; H, 9.03. Found: C, 74.35; H, 8.85.

Band 2 and the mother liquor from the crystallization of **6** were combined and rechromatographed (plate) on silica gel using chloroform–2% methyl alcohol as the developing solvent to give three poorly separated bands which were detectable by iodine vapor. Elution of band 1 with ethyl acetate and crystallization from isopropyl ether gave additional **6** (14 mg, mp 143.5–144.5°). Elution of band 2 gave a mixture of **6** and **7** (infrared). Elution of band 3 and crystallization from isopropyl ether gave **7** (5 mg, mp 127–128°). The nmr and infrared spectra of **7** were identical with those of an authentic sample.

2-Oxa-4β,5β-oxido-17β-hydroxyandrostan-3-one (8). A.—The aqueous phase from the previous example was acidified and extracted with chloroform. The chloroform extracts were washed with 8% salt solution, dried and evaporated. Plate chromatography of the residue (1.02 g) on alumina using chloroform–3% methyl alcohol as the developing solvent gave a major band detectable by iodine vapor. Elution with ethyl acetate and crystallization of the residue from methyl alcohol–isopropyl ether gave **8** (123 mg, mp 231–233°). Recrystallization from methyl alcohol–isopropyl ether gave the analytical sample: mp 231–233°; $[\alpha]^{26}D$ +97°; λ 2.86 (OH) and 5.82 μ (lactone); τ 9.23 (s, 18-Me), 8.95 (s, 19-Me), 6.69 (s, 4-H), 6.33 (m, 17-H) and 6.00 (poorly resolved quartet, 1-CH_2).

Anal. Calcd for $C_{18}H_{26}O_4$ (306.39): C, 70.56; H, 8.55. Found: C, 70.48; H, 8.56.

B.—A solution of A-nortestosterone (**3**, 1 g) in t-butyl alcohol (25 ml) and 4 N sodium hydroxide (2 ml) was treated with 30% hydrogen peroxide (4 ml) and stirred at room temperature for 3 days. Additional 30% hydrogen peroxide (4 ml) and 4 N sodium hydroxide (2 ml) were added and the stirring was continued for 3 additional days. The reaction mixture was diluted with water and extracted with ether. The aqueous phase was acidified and extracted with chloroform. The chloroform extracts were washed with 8% salt solution, dried, and evaporated. Crystallization of the residue from methyl alcohol–isopropyl ether gave **8** (448 mg, mp 220–221°).

C.—A solution of **6** (37 mg) in t-butyl alcohol (1 ml) and 4 N sodium hydroxide (0.2 ml) was cooled to −10° and treated with 30% hydrogen peroxide (0.4 ml). The reaction mixture was then stirred at room temperature for 2 days, diluted with water, and extracted with ether. The aqueous phase was acidified and extracted with chloroform. The chloroform extracts were washed with 8% salt solution, dried, and evaporated to give **8** (20 mg). The nmr and infrared of this sample were identical with those of an authentic sample. Plate chromatography on alumina using chloroform–2% methyl alcohol as the developing solvent gave a major band detectable by iodine vapor. Elution with ethyl acetate and crystallization from methyl alcohol–isopropyl ether gave **8** (7 mg, mp 230–232°). A mixture melting point with an authentic sample showed no depression.

3-Chloro-17β-acetoxy-A-norandrost-3-en-2-one (4) and 3-Methoxy-17β-acetoxy-A-norandrost-3-en-2-one (10).—A solution of A-nortestosterone (2 g) in methyl alcohol (20 ml) was oxidized as described previously and the crude reaction product refluxed for 2.5 hr in chloroform (50 ml) and ethyl alcohol (5 ml) saturated with hydrogen chloride. The reaction mixture was washed with saturated sodium bicarbonate solution, 8% salt solution, dried, and evaporated to give a 1.35-g residue. Plate chromatography of the residue on Florisil using chloroform–3% methyl alcohol as the developing solvent gave a major band detectable by ultraviolet light. Elution with ethyl acetate gave a residue which was refluxed in acetic anhydride (4 ml) and pyridine (0.4 ml) for 0.75 hr. The reaction mixture was poured into ice–water and extracted with ether. The ether extracts were washed with saturated sodium bicarbonate solution, 8% salt solution, dried, and evaporated. Plate chromatography of the residue on silica gel using chloroform–2% methyl alcohol as the developing solvent gave four major bands detectable by ultraviolet light.

Elution of band 1 with ethyl acetate and crystallization from isopropyl ether gave **4** (15 mg, mp 173–175°). Recrystallization from acetone–hexane gave the analytical sample: mp 175–177°; $[\alpha]^{27}D$ +26°; λ 5.80 (2-one) and 6.13 μ (C=C); λ 246 mμ (ε 13,400); τ 9.14 (s, 18-Me), 8.78 (s, 19-Me), 7.95 (s, 17-acetate), and 5.39 (m, 17-H).

Anal. Calcd for $C_{20}H_{27}ClO_3$ (350.87): C, 68.46; H, 7.76. Found: C, 68.35; H, 7.77.

Elution of bands 2 and 3 with ethyl acetate gave mixtures of **4** and **10** (infrared).

Elution of band 4 with ethyl acetate and crystallization from isopropyl ether gave **10** (45 mg, mp 135–137°). Recrystallization from acetone–petroleum ether (bp 30–60°) gave the analytical sample: mp 144–145°; λ 5.78 (acetate), 5.88 (2-one), and 6.06 μ (C=C); λ 250 mμ (ε 11,400); τ 9.15 (s, 18-Me), 8.85 (s, 19-Me), 7.96 (s, 17-acetate), 6.13 (s, 3-OMe), and 5.39 (m, 17-H).

Anal. Calcd for $C_{21}H_{30}O_4$ (346.45): C, 72.80; H, 8.73. Found: C, 72.93; H, 8.81.

Acknowledgment.—The author wishes to thank Dr. A. I. Cohen for the nmr spectra and valuable discussions.