174° and giving a brown-red color with ferric chloride. The melting point of this compound was not depressed by admixture of authentic 3,5-dinitro-2-hydroxybenzoic acid.[12] The infrared spectra of the two compounds were indistinguishable.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS, THE STATE UNIVERSITY]

Synthesis of Hydrochrysenes. I. 1-Methoxy-10-keto-3,4,5,6,7,8,10,11,12,12a-decahydrochrysene from 1,7-Dimethoxynaphthalene

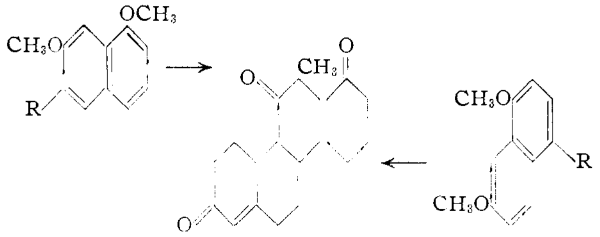
BY RODERICK A. BARNES AND WALTER M. BUSH[1]

RECEIVED APRIL 3, 1958

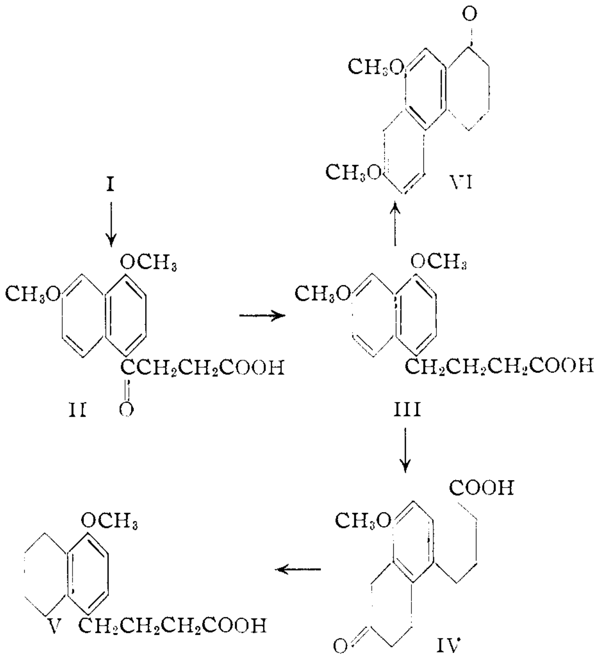
One of two possible synthetic routes from 1,7-dimethoxynaphthalene (I) toward 19-norsteroids with an oxygen function at position 11 has been investigated. The Friedel–Crafts reaction with succinic anhydride was observed to take place at the 4-position of I; further transformations of this reaction product led ultimately to 1-methoxy-10-keto-3,4,5,6,7,8,10,11,12,12a-decahydrochrysene.

Various modifications of a normal steroid structure such as addition of a 9-halogen atom or a 1,2-double bond and expansion of the D ring, have produced substances with enhanced biological activity. However, the structural modification in which the angular methyl group at position 19 is lacking cannot be accomplished in any simple way starting from the corresponding natural steroid. The reduction of estrone and related substances with an aromatic A ring, and subsequent transformations of the reduced product has been the most useful procedure for the preparation of 19-norsteroids.[2,3]

The experiments reported here were carried out to explore a possible synthetic route to the 19-norsteroids having an oxygen function at position 11. 1,7-Dimethoxynaphthalene (I) was chosen as the starting material, because, depending on the position which an entering substituent R might take, compound I could provide either rings C and D or B and C with the desired oxygen function properly located for either synthetic path.



The first substitution attempted with I was the Friedel–Crafts reaction with succinic anhydride. It seemed most likely that the bulky entering group, the succinic anhydride–aluminum chloride complex solvated with nitrobenzene, would react largely at the 4-position. The reaction product II was in fact mainly a single isomer and the small amount of acidic by-product was removed readily by recrystallization of II as the methyl ester. The reduction of the keto group of II by the Wolff–Kishner method produced considerable amounts of tarry products and a maximum of 25% of III; however, catalytic hydrogenation and hydrogenolysis using palladium-on-charcoal was nearly quantitative.



From III the ultimate synthetic goal could be achieved either by cyclization to VI or reduction to IV. Attempts to reduce III with sodium and alcohol failed, perhaps because of insolubility of the sodium salt. Reduction with lithium in liquid ammonia produced only 10% of IV. Although this route did not appear promising for the synthesis, the small amount of IV obtained provided a structure proof for II; Wolff–Kishner reduction of IV yielded acid V which was identical with a sample prepared by the method of Bachmann and Ness.[4] An attempt to prove the structure of II directly by oxidation was unsuccessful; the crystalline methyl ester of 4-methoxy-1,3,5-benzenetricarboxylic acid could not be isolated when the crude acidic oxidation product was treated with diazomethane.

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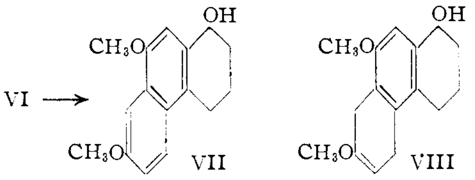
(1) Abstracted from a portion of the thesis presented by W. M. Bush to the Graduate Faculty for the Ph. D. degree, May, 1955.

(2) A. J. Birch, *J. Chem. Soc.*, 367 (1950); B. J. Magerlein and J. A. Hogg, THIS JOURNAL, **79**, 1508 (1957); F. B. Colton, L. N. Nysted, B. Riegel and A. L. Raymond, *ibid.*, **79**, 1123 (1957); A. Bowers, H. J. Ringold and R. I. Dorfman, *ibid.*, **79**, 4556 (1957).

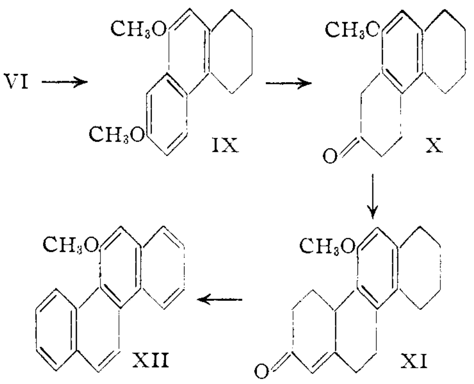
(3) For an approach to the synthesis of 19-norsteroids from a derivative of strophanthidin see G. W. Barber and M. Ehrenstein, *J. Org. Chem.*, **19**, 365 (1954).

(4) W. Bachmann and A. B. Ness, THIS JOURNAL, **64**, 536 (1942).

The preparation of VI was carried out by treating the acid chloride of III with stannic chloride in tetrachloroethane. It was anticipated that the carbonyl group of VI might be protected during subsequent conversion steps by conversion to the ethylene glycol ketal, but this derivative was not formed in appreciable amounts by the usual procedure. As an alternative, the preliminary reduction of the carbonyl group of VI was accomplished with lithium aluminum hydride to yield the expected alcohol VII. Unfortunately VII suffered cleavage of the alcoholic carbon–oxygen bond during the next step, the sodium and alcohol reduction of potential ring B. The method used to test for the presence of the desired reduction product VIII was oxidation with manganese dioxide in chloroform; the resulting oil had no absorption band at 6.03 μ (carbonyl group conjugated with benzenoid ring). When VII was oxidized in this way the product had the expected absorption band, but was not identical with VI, the expected product. The infrared spectrum of this material suggested that it might be a complex of VI and VII and this was verified by preparation of an identical substance merely by mixing equal amounts of VI and VII.



The steps involved in adding ring A were examined by reducing VI catalytically to IX which then was reduced further with sodium and alcohol.



When ketone X was treated with 4-diethylamine-2-butanone, the tetracyclic ketone XI was formed in about 30% yield. Although the most stable anion from X would be expected to react producing the desired product XI, there are some examples in which β-tetralones react abnormally.[5] Structure XI was proved to be the correct formulation for the tetracyclic ketone by reduction, dehydration and dehydrogenation to 1-methoxychrysene which was identical with an authentic sample.[6,7]

Experimental[8]

β-(1,7-Dimethoxy-4-naphthoyl)-propionic Acid (II).—Anhydrous aluminum chloride (106.4 g) was added in portions to a stirred solution of 1,7-dimethoxynaphthalene (67.7 g.) and succinic anhydride (40 g.) in tetrachloroethane (400 ml.) at 0–5°. After 12 hours the solution became very viscous and stirring was discontinued, but the reaction was maintained at *ca.* 0° for an additional 44 hours. The reaction mixture was decomposed with ice and hydrochloric acid and then steam distilled to remove the solvent. The crude solid acid was filtered and purified by redissolving in sodium carbonate solution, treating with Norite and finally acidifying the clear filtered solution of the sodium salt. The product obtained in this way (92 g., 90%) melted at 189–195°.

The acid was dissolved in dioxane and this solution was added to an ice-cold ether solution of diazomethane, prepared from nitrosomethylurea (79 g.). The excess diazomethane was decomposed by the addition of small amounts of acetic acid and the solvents were removed to yield an oil which could be crystallized from aqueous methanol. There was obtained 58 g. (64%) of the methyl ester which melted at 80–83°; one recrystallization raised the melting point to 82.5–84.5° (47.9 g.). The analytical sample melted at 84–85.5°.

Anal. Calcd. for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00. Found: C, 67.46; H, 6.06.

The saponification of this ester (47.9 g.) was accomplished by heating on the steam-bath with ethanol (130 ml.) and 10% aqueous potassium hydroxide solution (250 ml.) for 30 minutes. The solution was treated with charcoal, filtered and acidified. Recrystallization from aqueous acetic acid produced nearly colorless needles of acid II (43.6 g., 95%) which melted at 197.5–199.5°. The analytical sample melted at 198–199.5°.

Anal. Calcd. for $C_{16}H_{16}O_5$: C, 66.65; H, 5.60. Found: C, 66.68; H, 5.51.

γ-(1,7-Dimethoxy-4-naphthyl)-butyric Acid (III). A.—A mixture of potassium hydroxide (5 g.), diethylene glycol (20 ml.), 85% hydrazine hydrate (4.8 g.) and acid II (5 g.) was heated at reflux under nitrogen for an hour and then water was distilled until the temperature of the solution reached 185°. This temperature was maintained for 1.5 hours and then the solution was cooled and treated with ice and hydrochloric acid. The yellow product (4.5 g.) melted at 155–163° and after six recrystallizations from aqueous acetic acid there was obtained 1.2 g. (25%) of pure III which melted at 172–174°. The analytical sample, prepared by sublimation, melted at 173–174.5°.

Anal. Calcd. for $C_{16}H_{18}O_4$: C, 70.05; H, 6.61. Found: C, 70.20; H, 6.86.

Attempts to improve the yield by increasing the temperature or the reaction time only increased the amount of tarry by-products.

B.—Acid II (5 g.) was dissolved in acetic acid (50 ml.) containing a few drops of concentrated hydrochloric acid and reduced with hydrogen and 10% palladium-on-charcoal. The reaction was complete in three hours and the product was isolated by filtration and evaporation of the solvents at reduced pressure. The colorless reduction product was recrystallized from aqueous acetic acid to yield 4.1 g. (86%) of acid III which melted at 172–174° and was identical with the product obtained in part A.

γ-(1-Methoxy-7-keto-5,6,7,8-tetrahydro-4-naphthyl)-butyric Acid (IV).—Acid III (2.0 g.) was added to liquid ammonia (50 ml.) producing a white slurry of the ammonium salt. Lithium metal (0.4 g.) was added during 5 minutes and stirring was continued for an additional 10 minutes. Finally, absolute ethanol (5 ml.) was added dropwise during 15 minutes. The ammonia was allowed to evaporate and water (50 ml.) was added. Acidification of the aqueous solution produced a pinkish precipitate which was refluxed for 15 minutes with ethanol (10 ml.) and 6 *N* hydrochloric acid (5 ml.). The organic product was isolated by addition of water and extraction with benzene. The benzene solution was shaken for 24 hours with saturated bisulfite

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(5) M. D. Soffer, R. A. Stewart and G. L. Smith, THIS JOURNAL, **74**, 1556 (1952).

(6) R. A. Barnes and M. A. Manganelli, *ibid.*, **74**, 5826 (1952).

(7) J. Cook and R. Schoental, *J. Chem. Soc.*, 288 (1945).

(8) All melting points were determined with either a Kofler hot-stage or a Fisher–Johns melting point apparatus. Microanalyses were by W. Manser, Zurich, Switzerland, and George Robertson, Florham Park, N. J.

solution to yield 170 mg. of the bisulfite addition product. The addition product was dissolved in dilute sodium carbonate and this solution acidified to yield crude acid IV. Two recrystallizations from aqueous ethanol produced 40 mg. of pure IV which melted at 125–127°.

Anal. Calcd. for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.61; H, 7.05.

γ-(1-Methoxy-5,6,7,8-tetrahydro-4-naphthyl)-butyric Acid (V).—Acid IV (30 mg.) was reduced using potassium hydroxide (0.5 g.), 85% hydrazine hydrate (0.2 ml.) and diethylene glycol (2 ml.) as described for the preparation of III, part A, keeping the temperature at 180 ± 5° for four hours. The crude product was chromatographed on silica gel; benzene–ether (9:1) eluted the major fraction which melted at 118–123°. Recrystallization of this product from aqueous methanol raised its melting point to 122–124°. An authentic sample of acid V, prepared from 5-methoxytetralin and succinic anhydride by the method of Bachmann and Ness,[4] melted at 123.5–125°. A mixture of the two samples melted at the same temperature.

1-Keto-7,9-dimethoxy-1,2,3,4-tetrahydrophenanthrene (VI).—Phosphorus pentachloride (0.84 g.) and acid III (1.0 g.) were mixed and allowed to stand at room temperature for 1.5 hours. Dry chloroform (5 ml.) was added and the mixture warmed until all of the solids were in solution. The solution was allowed to stand for a half hour and then dry benzene (20 ml.) was added and removed under reduced pressure. Finally the acid chloride was heated at 100° at 10 mm. for an hour. Anhydrous aluminum chloride (0.8 g.) was added to a solution of the acid chloride in nitrobenzene (6 ml.) at 0°. The reaction mixture was kept in an ice-bath for seven hours and then decomposed with ice and hydrochloric acid. The solvent was steam distilled and the product extracted with benzene. The extracts were washed with sodium bicarbonate solution to remove acidic materials. The residual oil obtained after evaporation of the benzene, was crystallized by stirring with hexane and then recrystallized from hexane–acetone. There was obtained 0.62 g. (65%) of VI which melted at 133–135°. The analytical sample, prepared by sublimation, melted at 134–135°; $\lambda_{max}^{CHCl_3}$ 6.03, 6.20 and 6.25 μ.

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.65; H, 6.32.

When this ketone was heated with benzene, ethylene glycol and *p*-toluenesulfonic acid for 60 hours, removing any water formed azeotropically, only *ca.* 1% of crystalline material (m.p. 141–147°) was obtained which had no carbonyl absorption bands in the infrared spectrum; most of the starting material was recovered unchanged.

1-Hydroxy-7,9-dimethoxy-1,2,3,4-tetrahydrophenanthrene (VII).—A mixture of ketone VI (2.69 g.) and lithium aluminum hydride (1.35 g.) in dry ether (50 ml.) was refluxed for 8 hours. The excess hydride was destroyed with ethyl acetate and ammonium chloride solution was added to decompose the complex. The ether was separated and the solid residue washed with ether. Evaporation of the combined ether solutions left a solid residue which was recrystallized from benzene–hexane to yield 2.39 g. (89%) of VII which melted at 120–122° with some preliminary softening at 118°. Further recrystallization did not change the melting behavior and since the reduction was complete (no carbonyl absorption in the infrared), it is believed that VII was dehydrated readily even during recrystallization. The analysis also indicated that some dehydrated product was present in this sample of VII, $\lambda_{max}^{CHCl_3}$ 2.95 and 6.25 μ.

Anal. Calcd. for $C_{16}H_{18}O_3$: C, 74.40; H, 7.02. Found: C, 75.41; H, 6.70.

When VII was oxidized with manganese dioxide[9] in chloroform[10] and the solid product recrystallized from hexane–benzene, a homogeneous substance was obtained which melted at 130–132.5°. The melting point of a mixture with pure VI was 122–130°. The infrared spectrum indicated that both a hydroxyl and a carbonyl group were present ($\lambda_{max}^{CHCl_3}$ 2.95, 6.02 and 6.24 μ). When a 1:1 mixture of VI and VII was recrystallized from hexane–benzene, a crystalline substance which melted at 129–132° was obtained; this material was identical with that from the oxidation by the criterion of the mixture melting point.

Attempted Reduction of VII.—Sodium (1.5 g.) was added in small pieces to a refluxing solution of VII (407 mg.) in absolute ethanol (10 ml.) during an hour. The cold reaction mixture was diluted with water and the product extracted with ether; evaporation of the ether left a colorless oil whose infrared spectrum showed only slight absorption in the hydroxyl region ($\lambda_{max}^{CHCl_3}$ 6.10 and 6.25 μ). Oxidation with manganese dioxide as for VII yielded an oil whose infrared spectrum had olefinic and aromatic absorption bands at 6.09 and 6.27 μ, respectively, but lacked the conjugated carbonyl band expected at *ca.* 6.03 μ. A weak band at 5.85 μ indicated that some of the enol ether produced on reduction had hydrolyzed to yield the corresponding β-tetralone with an unconjugated carbonyl group.

7,9-Dimethoxy-1,2,3,4-tetrahydrophenanthrene (IX).—Alcohol VII (1.51 g.) in absolute ethanol (50 ml.) containing a few drops of concentrated hydrochloric acid was reduced with hydrogen (3 atmospheres) and in the presence of 10% palladium-on-charcoal. The reaction was complete in three hours. The solution was filtered, the solvent removed and the crude product chromatographed on alumina. The fractions eluted with pure hexane and 5% benzene in hexane were combined and recrystallized from benzene to yield 1.17 g. (83%) of colorless platelets which melted at 85.5–87°.

Anal. Calcd. for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.61; H, 7.44.

2-Keto-10-methoxy-1,2,3,4,5,7,8-octahydrophenanthrene (X).—Compound IX (500 mg.) was reduced with sodium (1.5 g.) and absolute ethanol (12 ml.) using the same procedure as for VII. The crude enol ether (475 mg.) in ethanol solution (10 ml.) was warmed on the steam-bath with 1 *N* hydrochloric acid (7 ml.) for a half-hour. When the reaction mixture was cooled a crystalline product (375 mg.) separated; this substance was purified by chromatography on silica gel. The fraction eluted with 5% ether in benzene (340 mg.) melted at 105–110°, $\lambda_{max}^{CHCl_3}$ 5.82 and 6.25 μ. This fraction was analyzed without further purification.

Anal. Calcd. for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 77.54; H, 7.63.

1-Methoxy-10-keto-3,4,5,6,7,8,10,11,12,13-decahydrochrysene (XI).—A solution of compound X (450 mg.) in benzene (3 ml.) was added to a slurry of freshly prepared sodamide in benzene (3 ml.). This mixture was stirred vigorously for 15 minutes at 0° and the methiodide salt prepared from 4-diethylamino-2-butanone (292 mg.) by the method of Wilds and Shunk[11] was added in dry isopropyl alcohol (3 ml.). The reaction was completed by stirring at 0° for a half-hour and finally at reflux temperature for an additional half-hour.

The reaction product was isolated by addition of 2 *N* sulfuric acid to the cold mixture and benzene extraction of the organic product. The oil remaining after washing and concentrating the benzene solution was chromatographed on silica gel. The fraction eluted with 3% ether in benzene crystallized and after recrystallization from methanol afforded material (176 mg.) which melted at 148–154°. Further chromatography yielded a pure fraction (72 mg.) which melted at 157–159° after recrystallization from hexane–acetone; $\lambda_{max}^{CHCl_3}$ 6.03, 6.15 and 6.26 μ.

Anal. Calcd. for $C_{19}H_{22}O_2$: C, 80.81; H, 7.86. Found: C, 80.55; H, 7.97.

A sample of XI (40 mg.) was reduced with lithium aluminum hydride as in the preparation of VII. The crude product was dehydrated and dehydrogenated by heating at 280° under nitrogen with 10% palladium-on-charcoal and 2,6-dimethylnaphthalene (1 ml.). The reaction mixture was diluted with hexane, filtered and chromatographed on alumina. The 2,6-dimethylnaphthalene was eluted with hexane and the product (10.7 mg.) with 40% benzene in hexane; the movement of the 1-methoxychrysene down the column could be followed readily in ultraviolet light. Further purification of this substance by sublimation yielded colorless crystals (5 mg.) which melted at 143–144.5°.

An authentic sample of 1-methoxychrysene was prepared by a similar procedure from a sample of 1-methoxy-3-keto-1,2,3,4-tetrahydrochrysene.[12] This process, involving re-

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(9) Kindly furnished by Dr. H. M. Fales, National Institutes of Health, Bethesda, Md.

(10) J. Attenburrow, A. Cameron, J. Chapman, R. Evans, B. Hems, A. Jansen and T. Walker, *J. Chem. Soc.*, 1094 (1952).

(11) A. L. Wilds and C. H. Shunk, THIS JOURNAL, **65**, 471 (1943).

(12) Prepared by M. A. Manganelli, ref. 6.

duction only to the alcohol stage prior to dehydrogenation, is much more efficient than the previously reported method *via* the Clemmensen reduction of the ketone group.[6] This sample melted at 144–146° alone or when mixed with that prepared from ketone XI.

NEW BRUNSWICK, N. J.

[CONTRIBUTION OF THE RESEARCH LABORATORIES, THE UPJOHN CO.]

6-Methyl Steroids in the Androstane Series[1]

BY J ALLAN CAMPBELL, JOHN C. BABCOCK AND JOHN A. HOGG

RECEIVED MARCH 27, 1958

Methylmagnesium bromide cleaved the epoxy group of 3-hydroxy- and 3-ethylenedioxy-$5\alpha,6\alpha$-epoxyandrostanes to give the corresponding 5α-hydroxy-6β-methyl derivatives. Dehydration of the 3-keto-5α-hydroxy intermediates afforded 6β-methylandrostenedione, testosterone, methyltestosterone and ethinyltestosterone, while dehydration and isomerization gave the corresponding 6α-methyl compounds.

An earlier communication from these laboratories[2] described 6-methyl derivatives of the cortical hormones and the potentiating effect of this modification on biological activity. This paper is a continuation of these studies and describes the 6-methylandrostenes.

More than seventeen years ago Madaeva, Ushakov and Kosheleva[3] synthesized 6α-methyl-4-androstene-3,17-dione without assigning a configuration to the 6-methyl group. The androgenic activity was reported to be about the same as that of the parent compound. During the preparation of this manuscript a preliminary announcement by Ringold, *et al.*,[4] and a more detailed study by Petrow, *et al.*,[5] appeared describing portions of the material covered in this work.

The 6-methyl group was introduced into the steroid molecule by cleavage of the $5\alpha,6\alpha$-epoxides with methylmagnesium bromide. High yields of cleavage products were obtained from 3-ethylenedioxy-$5\alpha,6\alpha$-epoxides. However, when a 3-hydroxyl or a 3-acetoxyl group was present the $5\alpha,6\alpha$-epoxide was cleaved with some difficulty.

Thus, although $5\alpha,6\alpha$-epoxyandrostane-$3\beta,17\beta$-diol (Ib) was treated with methylmagnesium bromide in boiling tetrahydrofuran for 24 hours, the product (m.p. 115–120°, lit.[3] m.p. 117–120°), which seemed to be a dihydrate of IIb by analysis and infrared absorption, was shown to contain a considerable amount of starting material. Chromium trioxide oxidation of the crude Grignard product gave a mixture of ketones which could not be separated by chromatography over Florisil. Evidence that the Grignard reaction (Ib $\rightarrow$ IIb) did not proceed to completion was obtained by treating the crude oxidation product with piperidine and chromatographing the resulting mixture to give 6α-hydroxy-4-androstene-3,17-dione (Xa)[6a] (presumably arising from $5\alpha,6\alpha$-epoxyandrostane-3,17-dione (IXa)) along with the expected 5α-hydroxy-6β-methyl-3-ketone IIIa. Although the 6α-hydroxyandrostenedione (Xa) melted somewhat higher than reported,[6b] its structure was confirmed both by acetylation to the 6α-acetate and by isomerization to the 3,6-dione. Further evidence that the Grignard reaction (Ib $\rightarrow$ IIb) did not proceed to completion was obtained by treating the crude reaction product with *p*-toluenesulfonic acid in pyridine. The acetone-insoluble pyridinium salt XIIb thus produced could be separated from the 5α-hydroxy-6β-methyl compound IIb and reverted to the starting epoxide Ib by treatment with alcoholic potassium hydroxide.

The reaction of methylmagnesium bromide with $5\alpha,6\alpha$-epoxy-17α-methylandrostane-$3\beta,17\beta$-diol (Ic) and its 3-acetate gave products of variable melting points (165–190°) and rotations (−41 to −52°).[7] Recrystallization gave less than 40% yield of the triol IIc, m.p. 205–215°, having a characteristic strong hydrate band at 1635 $cm.^{-1}$ in the infrared spectrum. Analysis indicated it to be a monohydrate. Oxidation of the triol IIc with chromium trioxide in acetic acid gave the corresponding 3-ketone IIIc in about 50% yield.

The reaction of the epoxides of androstenedione-3-ketal (Va), testosterone ketal (Vb) and methyltestosterone ketal (Vc) with methylmagnesium bromide in boiling tetrahydrofuran proceeded without difficulty in yields of 70–85%. Although some of the 5-hydroxy-6-methyl-3-ketals resisted crystallization, after removal of the ketal groups in dilute acidic methanol nicely crystalline products (IIIa, b, c and d) were obtained.

The epoxide of testosterone ketal (Vb) was a convenient intermediate since it was prepared easily, and from it the whole series of 6-methyl C_{19}-steroids could be made. Thus, it reacted with methylmagnesium bromide to give the 5α-hydroxy-6β-methyl intermediate VIb which, after removal of the ketal and dehydration, gave the 6-methyltes-

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(1) Presented before the Division of Organic Chemistry at the 132nd Meeting of the American Chemical Society, New York, N. Y., September 8–13, 1957.

(2) G. B. Spero, J. L. Thompson, B. J. Magerlein, A. R. Hanze, H. C. Murray, O. K. Sebek and J. A. Hogg, THIS JOURNAL, **78**, 6213 (1956).

(3) O. S. Madaeva, M. I. Ushakov and N. F. Kosheleva, *J. Gen. Chem.* (*USSR*), **10**, 213 (1940); *C. A.*, **34**, 7292 (1940).

(4) H. J. Ringold, E. Batres and G. Rosenkranz, *J. Org. Chem.*, **22**, 99 (1957).

(5) M. Ackroyd, W. J. Adams, B. Ellis, V. Petrow and I. A. Stuart-Webb, *J. Chem. Soc.*, 4099 (1957); V. Greenvill, D. K. Patel, V. Petrow, I. A. Stuart-Webb and D. M. Williamson, *ibid.*, 4105 (1957); G. Cooley, B. Ellis, D. N. Kirk and V. Petrow, *ibid.*, 4112 (1957).

(6) (a) C. P. Balant and M. Ehrenstein, *J. Org. Chem.*, **17**, 1587 (1952). (b) We are very grateful to Prof. Ehrenstein for determining a "mixed melting point"; there was no depression.

(7) Reference 4 gives m.p. 191–192° and $[\alpha]_D$ −45° and states that satisfactory analysis could not be obtained apparently due to solvent of crystallization.