a crystalline material which was filtered, washed well with water, and dried to give III (8.56 g., 94%), m.p. 98–107°. Chromatography on silica gel and recrystallization from methanol gave an analytical sample having m.p. 142–143°, λ^{KBr} 2.85, 5.88, 6.85, 7.22, 9.00, 9.75, 9.98, and 10.23 μ, $[\alpha]_D$ −41° (*c* 1, $CHCl_3$). III exhibited no distinct ultraviolet absorption.

Anal. Calcd. for $C_{25}H_{40}O_3$: C, 77.27; H, 10.38. Found: C, 77.10; H, 10.51.

4,4,6,16α-Tetramethyl-5-androstene-3,17-dione (IV).—4,4,6,-16α-Tetramethyl-5-pregnene-17α,20β-diol-3-one (III) (300 mg.) was dissolved in 30 ml. of methanol and treated with an aqueous solution of 250 mg. of periodic acid in 5 ml. of water at room temperature for 17 hr. On dilution with water, the resultant crystals were collected by filtration, washed well with water, and dried to give 262 mg. of crystals, m.p. 158–160°. Recrystallization from hexane–acetone gave 240 mg. of IV, m.p. 160–161°, λ^{KBr} 5.80, and 5.88 μ, $[\alpha]^{25}_D$ −6° (*c* 1, $CHCl_3$). Mass spectrum showed a strong *m/e* 342 peak.

Anal. Calcd. for $C_{23}H_{34}O_2$: C, 80.65; H, 10.00. Found: C, 80.59; H, 9.96.

4,4,6,16α-Tetramethyl-5-androstene-17β-ol-3-one (V).—4,4,-6,16α-Tetramethyl-5-androstene-3,17-dione (IV) (175 mg.) was dissolved in 30 ml. of absolute methanol and the system was flushed with nitrogen gas for 3 min. Sodium borohydride (40 mg.) was then added and the mixture stirred for 30 min. at room temperature. A few drops of acetic acid were added and the mixture diluted with water. The resulting crystals were collected by filtration, washed well with water, and dried to give 174 mg. of crystals, m.p. 96–99°. Recrystallization from aqueous methanol furnished pure 4,4,6,16α-tetramethyl-5-androstene-17β-ol-3-one (V), 162 mg. of crystals, m.p. 101–102°, λ^{KBr} 2.90, and 5.85 μ, $[\alpha]_D$ −42° (*c* 1, $CHCl_3$). V exhibited no significant ultraviolet absorption.

Anal. Calcd. for $C_{23}H_{36}O_2$: C, 80.18; H, 10.53. Found: C, 80.12; H, 10.47.

4,4,6,16α-Tetramethyl-5-androstene-3β,17β-diol (VI).—A solution of 4,4,6,16α-tetramethyl-5-androstene-3,17-dione (IV) (235 mg.) in 30 ml. of anhydrous ether was added at ambient temperature during a period of 15 min. to a stirred solution of lithium aluminum hydride (300 mg.) in 30 ml. of anhydrous ether. The mixture was then refluxed for 30 min., cooled to 0°, and excess lithium aluminum hydride decomposed with water. The mixture was further diluted with water and extracted with ethyl acetate. The organic layer was washed well with water, dried over magnesium sulfate, filtered, and concentrated to give 228 mg. of crystals, m.p. 105–118°, which was put on a 5 g. Florisil column. Elutions with hexane gave crude crystals (164 mg.) m.p. 109–121°. Recrystallization of 156 mg. of crude product from hexane–acetone gave a first crop of 62 mg. of crystals, m.p. 120–121°, λ^{KBr} 3.00, no carbonyl absorption, 9.45, and 9.88 μ. There was no significant ultraviolet absorption. The mass spectrum showed a parent peak corresponding to molecular weight of 346, and M − CH_3, M − H_2O, M − (CH_4 + H_2O) and strong M − 83 peaks have been observed.

Anal. Calcd. for $C_{23}H_{38}O_2$: C, 79.71; H, 11.05. Found: C, 79.68; H, 11.03.

16α-Fluorinated Steroids from the Reaction of Perchloryl Fluoride with Enamides[1]

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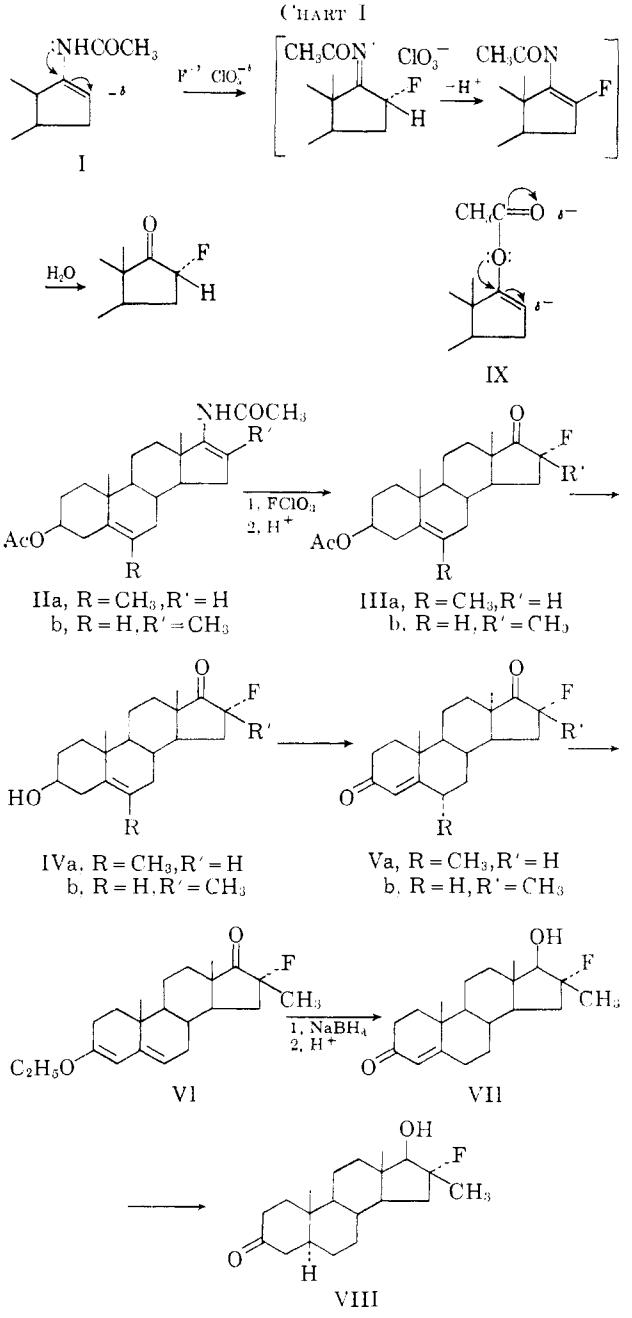
The reaction of perchloryl fluoride with enamines,[2,3] enol ether,[4] and enol ester[5] derivatives of saturated and 4,5-unsaturated 3-ketosteroids provides a convenient method for the introduction of a fluorine substituent adjacent or vinylogous to the carbonyl group. Application of these reactions to 17-ketosteroids has been limited by the reluctance of the 17-ketone to form enol ethers[1] or enamines.[1,6,7]

We have found that acetylated 17-amino-Δ^{16}-steroids (enamides), conveniently prepared[8] by the Beckmann rearrangement of the oxime of 20-keto-Δ^{16}-steroids, react smoothly and stereospecifically with perchloryl fluoride to furnish the corresponding 16α-fluoro-17-ketosteroids in high yield.[1]

Presumably, the reaction proceeds by electrophilic attack of the fluorine at the negative center at position C-16 (I) followed by loss of a proton to produce a

CHART I



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fluorinated acetyl amine. Subsequent addition of water results in rapid hydrolysis to the fluorinated ketone as illustrated in Chart I. In direct contrast, the fluorination reaction of perchloryl fluoride with the enol acetate (IX) of a 17-ketosteroid is very slow and is accompanied by side reactions of chlorination.[1] The greatly enhanced reactivity of the acetylamino compound (I) as compared to the enol ester (IX) is consistent with the greater ability of the nitrogen atom to donate electrons to the double bond for interaction with the electrophilic fluorine of perchloryl fluoride.

A brief treatment of enamides II in pyridine with perchloryl fluoride at room temperature furnished 16α-fluoro-3β-acetoxy-5-androstene-17-one derivatives (III) in 70% yield. Acidic methanolysis of III gave the corresponding 3β-hydroxy compounds (IV) in quantitative yield. Oxidation of IV by chromic acid in acetone gave rise to 71% of 16α-fluoro-4-androstene-3,17-dione derivatives (V). Configuration assignment of α-fluorine and β-methyl groups for 16α-fluoro-16β-methyl-4-androstene-3,17-dione (Vb) has been performed by infrared spectrum[9a] as well as by n.m.r. study[9b] which is in agreement with the observations of Cross and Landis.[10] Vb was further converted to its 3-ethoxy enol ether (VI) and reduced with sodium borohydride to 16α-fluoro-16β-methyltestosterone (VII). Direct partial reduction[11] of Vb gave rather poor yield, due to 3,17-diol formation in spite of the expected difference in the reactivity between 17-ketone and the 4-en-3-one.[11] Reduction of VI with either sodium borohydride or lithium aluminum hydride produced VII with retention of configuration at C-16. Catalytic hydrogenation of VII gave 16α-fluoro-16β-methyldihydrotestosterone (VIII).

In both compounds, VII and VIII, androgenic properties[12] (ventral prostate) were of a low order at both 0.14 and 1.4 mg. total dose levels, being about 10% that of testosterone and similar to the control, while the seminal vesicles weight increase was only about three times the control, and almost no change of levator ani was observed. Similar observations have been described recently by Hoffman and his co-workers[13] on 16-disubstituted progesterone and deoxycorticosterone derivatives.

Experimental[14]

6-Methylpregna-5,16-dien-3β-ol-20-one 3-Acetate 20-Oxime.—6-Methyl-pregna-5,16-diene-3β-ol-20-one 3 acetate was converted to its 20-oxime in quantitative yield according to the method of Rosenkranz, *et al.*[8] The analytical sample was recrystallized from hexane–acetone and melted at 202–203°, $[\alpha]^{25}D$ −53.0°, λ^{KBr} 2.90, 5.79, 6.20, 6.29, 7.85, and 12.19 μ.

Anal. Calcd. for $C_{24}H_{35}NO_3$: C, 74.76; H, 9.15; N, 3.63. Found: C, 74.69; H, 9.21; N, 3.62.

6-Methyl-3β-acetoxy-17-acetamino-5,16-androstadiene (IIa).—The Beckmann rearrangement[8] of the above 20-oxime furnished slightly orange colored crystals of IIa, 4.67 g. (88%), m.p. 196–198° dec., $[\alpha]^{27}D$ −45.7°, λ^{KBr} 3.02, 3.41, 5.78, 6.04, 6.49, 7.28, 8.00, and 12.22 μ.

Anal. Calcd. for $C_{24}H_{35}NO_3$: C, 74.65; H, 9.34; N, 3.75. Found: C, 74.76; H, 9.15; N, 3.63.

6-Methyl-16α-fluoro-5-androsten-3β-ol-17-one 3-Acetate (IIIa).—The enamide IIa (4 g.) was dissolved in 250 ml. of dry pyridine and treated with perchloryl fluoride at room temperature for 4 min. After removal of excess perchloryl fluoride by water pump suction, the reaction mixture was poured into ice–water, acidified with concentrated hydrochloric acid to pH 2, and the acidic suspension was kept at room temperature for 15 hr. to complete the hydrolysis. The crystalline solids were filtered, well washed with water, and dried *in vacuo* overnight to give 3.58 g., m.p. 99–106°. Purification by Florisil column chromatography (elutions with methylene chloride) gave 2.708 g. (72% of crystals, m.p. 199–213°. Recrystallization from hexane–acetone gave 70% of IIIa, m.p. 214–215°, $[\alpha]^{25}D$ +8°, λ^{KBr} 5.70, 5.81, and 8.02 μ.

Anal. Calcd. for $C_{22}H_{31}FO_3$: C, 72.89; H, 8.62; F, 5.24. Found: C, 72.83; H, 8.46; F, 5.20.

6-Methyl-16α-fluoro-5-androsten-3β-ol-17-one (IVa).—A mixture of IIIa (1.4 g.) in 200 ml. of absolute methanol and 1 ml. of concentrated hydrochloric acid was kept at room temperature overnight. After concentration to about 10 ml., it was diluted with H_2O, filtered, washed, dried, and concentrated to give 1.233 g. of crystals, m.p. 134–140°. Two recrystallizations from hexane–acetone gave IVa, (1.185 g., 96%), m.p. 169–170.5°, $[\alpha]^{25}D$ +24°, λ^{KBr} 2.86 and 5.70 μ.

Anal. Calcd. for $C_{20}H_{29}FO_2$: C, 74.96; H, 9.12; F, 5.93. Found: C, 74.84; H, 9.56; F, 5.97.

6α-Methyl-16α-fluoro-4-androstene-3,17-dione (Va).—The chromic acid oxidation[8] of IVa (730 mg.) in acetone at 10°, followed by a purification on 15 g. of Florisil (elution with methylene chloride), gave 490 mg. of crystals, m.p. 178–184°. Recrystallization from hexane–acetone gave 370 mg. of crystals, m.p. 184–185°. Another recrystallization from the same solvent mixture furnished Va monohydrate (364 mg.), m.p. 227–228°, $[\alpha]^{28}D$ +119°, λ^{KBr} 5.69, 5.98, and 6.22 μ, λ_{max}^{EtOH} 241 mμ (ε 16,680).

Anal. Calcd. for $C_{20}H_{27}FO_2$: C, 71.40; H, 8.69; F, 5.65. Found: C, 71.60; H, 8.09; F, 5.58.

16-Methyl-5,16-pregnadiene-3β-ol-20-one 3-Acetate 20-Oxime.—16-Methyl-16-dehydropregnenolone acetate (5 g.) was converted to 16-methyl-5,16-pregnadiene-3β-ol-20-one 3-acetate 20-oxime (4.84 g., 92%), m.p. 176–177° (from hexane–acetone), $[\alpha]^{25}D$ −90.7°, λ^{KBr} 2.84, 5.82, 5.86, 6.16, and 6.27 μ.

Anal. Calcd. for $C_{24}H_{35}NO_3$: C, 74.76; H, 9.15; N, 3.63. Found: C, 74.65; H, 9.07; N, 3.66.

16-Methyl-17-acetylamino-5,16-androstadiene-3β-ol 3-Acetate (IIb).—The Beckmann rearrangement[8] of the above oxime (4.5 g.) gave IIb (3.395 g., 74%), m.p. 193–195° dec. (from hexane–acetone), λ^{KBr} 3.02, 5.76, 5.94, 6.52, 8.00, and 12.22 μ; $[\alpha]^{32}D$ −33.2°.

Anal. Calcd. for $C_{24}H_{35}NO_3$: C, 74.76; H, 9.15; N, 3.63. Found: C, 74.71; H, 9.04; N, 3.85.

16α-Fluoro-16β-methyl-5-androsten-3β-ol-17-one 3-Acetate (IIIb).—The enamide (IIb) (3.3 g.) was dissolved in 250 ml. of pyridine and treated with perchloryl fluoride at room temperature for 4 min. After removal of excess perchloryl fluoride by water-pump suction it was diluted with ice–water, acidified with concentrated hydrochloric acid to pH 2, and kept at room temperature for 5 hr. The crystals formed were filtered, washed with water to neutrality, and dried to give 3.019 g. of crystals, m.p. 94–102°. Purification by Florisil column chromatography (elutions with methylene chloride) gave 2.547 g. (80.5%) of crystals, m.p. 162–168°. Recrystallization from hexane–acetone gave IIIb (2.03 g.), m.p. 168–169°, $[\alpha]^{31}D$ +37.1°, λ^{KBr} 5.69, 5.79, and 8.04 μ.

Anal. Calcd. for $C_{22}H_{31}FO_3$: C, 72.89; H, 8.62; F, 5.24. Found: C, 73.18; H, 8.58; F, 5.01.

16α-Fluoro-16β-methyl-5-androsten-3β-ol-17-one (IVb).—A solution of IIIb (1.88 g.) in a mixture of 200 ml. of methanol and 1 ml. of concentrated hydrochloric acid was kept at room temperature overnight. Then it was diluted with water and the resulting crystals were filtered, washed, and dried to give 1.695 g. of crystals, m.p. 170–177°. The crude product 1.62 g. was purified by Florisil (60 g.) chromatography. Elution with methylene chloride containing 5% ether gave 1.07 g. of crystals,

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m.p. 173.5–178.5°. Recrystallization from acetone–hexane furnished IVb (1.05 g.), m.p. 176–178.5°, $[\alpha]D$ +43°, λ^{KBr} 2.93, 5.68 μ.

Anal. Calcd. for $C_{20}H_{29}FO_2$: C, 74.96; H, 9.12; F, 5.93. Found: C, 74.79; H, 9.14; F, 5.73.

16α-Fluoro-16β-methyl-4-androstene-3,17-dione (Vb).—The chromic acid oxidation[8] of IVb, 1 g., in acetone at 5° yielded 980 mg. of crystals, m.p. 198–202°. Recrystallization from ether gave Vb, 950 mg., m.p. 204–205°, λ_{max}^{EtOH} 241 mμ (ϵ 16,400), $[\alpha]D$ +203°, λ^{KBr} 5.69, 6.01, 6.20 μ.

Anal. Calcd. for $C_{20}H_{27}FO_2$: C, 75.43; H, 8.55; F, 5.97. Found: C, 75.66; H, 8.40; F, 5.77.

16α-Fluoro-16β-methyl-3-ethoxyandrost-3,5-diene-17-one (VI) and 16α-Fluoro-16β-methyl-androst-4-ene-17β-ol-3-one (VII). (a)—A mixture of Vb (950 mg.), 10 ml. of dry tetrahydrofuran and 0.6 ml. of triethyl orthoformate was heated to reflux. Then 0.4 ml. of absolute ethanol containing 2 drops of concentrated sulfuric acid was added. After refluxing for 30 min., an additional 0.4 ml. of triethyl orthoformate was added, then the mixture was refluxed for an additional hr. The mixture was then diluted with water, extracted with ethyl acetate, the organic layer was washed with water, dried over magnesium sulfate, filtered, and concentrated to give 1.1 g. of oil, λ^{CCl_4} 2.78, 6.04, and 6.13 μ. This crude oil was dissolved in 25 ml. of anhydrous tetrahydrofuran and then 8.2 ml. of water, 0.125 ml. of 2.5 *N* sodium hydroxide, and 520 mg. sodium borohydride were added with stirring, and the mixture was refluxed for 5 hr. After cooling to room temperature, the mixture was extracted with ethyl acetate, and the organic layer was washed to neutrality, dried, and concentrated to give 900 mg. of a foamy glaze. This crude product was dissolved in 30 ml. of absolute ethanol and 5.2 ml. of water. Then 10.5 ml. of 0.12 *N* hydrochloric acid was added and the mixture was kept at room temperature overnight. The mixture was further diluted with 300 ml. of water and extracted with ethyl acetate. The organic layer was washed with 5% sodium bicarbonate solution and water to neutrality, dried, and concentrated to give 800 mg. of foam, λ^{KBr} 2.91, 6.0, and 6.18 μ. Employing a 30 g. Florisil column, elutions with 10% ether in methylene chloride yielded 485 mg. of crystals, m.p. 128–133°. Recrystallization from ether gave a first crop of VII (315 mg.), m.p. 134–135°, $[\alpha]D$ +31°, λ_{max}^{EtOH} 241 mμ (ϵ 11,500), λ^{KBr} 2.92, 6.01, and 6.19 μ.

Anal. Calcd. for $C_{20}H_{29}FO_2$: C, 74.96; H, 9.12; F, 5.93. Found: C, 74.94; H, 9.10; F, 5.94.

(b).—A solution of 16α-fluoro-16β-methyl-3-ethoxyandrost-3,5-diene-17-one (350 mg.) in 30 ml. of anhydrous ether was added during a period of 15 min. to a stirred solution of 300 mg. of lithium aluminum hydride in 30 ml. of anhydrous ether. The mixture was refluxed for 30 min., cooled to 0°, and the excess lithium aluminum hydride was decomposed with water, diluted with water, and extracted with ethyl acetate. The organic layer was washed with water, dried, and concentrated to give 229 mg. of solid. The solids were redissolved in a mixture of 5 ml. of ethanol, 10 ml. of water, and 10 ml. of 0.1 *N* hydrochloric acid and then kept at room temperature overnight. Extraction with ethyl acetate followed by a Florisil column chromatography (elutions with methylene chloride) gave 166 mg. of crystals, m.p. 126–135°. Recrystallization from ether gave a first crop of VII (121 mg.), m.p. 134–135°, identical with the compound obtained by sodium borohydride reduction.

16α-Fluoro-16β-methyl-dihydrotestosterone (VIII).—A mixture of VII (250 mg.) in 10 ml. of ethanol and 31.3 mg. of 10% palladium on charcoal was hydrogenated at room temperature during a period of 25 min. The catalyst was removed by filtration and the filtrate was evaporated *in vacuo* to give 245 mg. of foam, λ^{KBr} 2.92, and 5.85 μ. The crude product was purified by Florisil (10 g.) chromatography. Elutions with methylene chloride containing 5% ether gave 180 mg. of crystals, m.p. 154–156°. Recrystallization from ether furnished the analytical sample of VIII, 120 mg., m.p. 156–157°, λ^{KBr} 2.92, and 5.85 μ.

Anal. Calcd. for $C_{20}H_{31}FO_2$: C, 74.49; H, 9.68; F, 5.89. Found: C, 73.82; H, 9.51; F, 5.85.

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A Tautomer of a 2-Thienol Analog of Stilbestrol[1,2]

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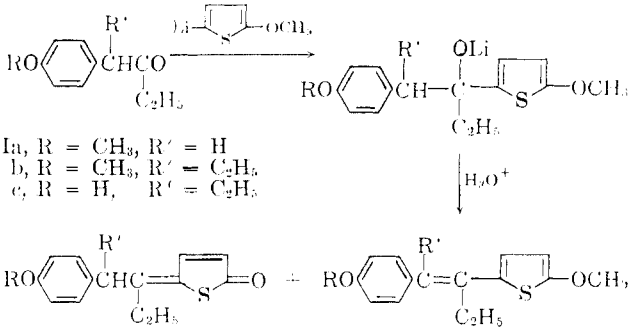
Following the discovery of the high estrogenic potency of diethylstilbestrol,[3] numerous related compounds were prepared for hormonal assay.[4] More recently the search has turned toward the development of compounds which might possess antihormonal action[5]; relatively few of these compounds have included heterocyclic groupings. However, several stilbestrol-like compounds bearing the thiophene nucleus in place of one or both of the benzene rings have been reported.[6]

In an attempt to prepare a 2-thienol analog of stilbestrol, we have now succeeded in synthesizing its more stable tautomeric α,β-unsaturated thiolactone form as the crystalline acetate, (IId). Preliminary work, resulting in the synthesis of the related methyl ethers (IIa and IIb), was also conducted. A recently developed synthesis[7] of 5-substituted 2(5*H*)-thiophenones has been utilized.



Ia, R = CH_3, R' = H
b, R = CH_3, R' = C_2H_5
c, R = H, R' = C_2H_5

IIa, R = CH_3, R' = H
b, R = CH_3, R' = C_2H_5
c, R = H, R' = C_2H_5
d, R = CH_3CO, R' = C_2H_5

IIIa, R = CH_3, R' = H
b, R = CH_3, R' = C_2H_5

Ketones Ia and Ib were prepared from the appropriate acyl chlorides and diethylcadmium or by the method of Myers, *et al.*[5a] The phenolic ketone (Ic) was prepared from α-(*p*-acetoxyphenyl)-butyryl chloride[8] and diethylcadmium, followed by hydrolysis (65% yield) or by hydrobromic acid demethylation of the methoxy ketone (Ib).

(1) This investigation was supported by a research grant, T-114, from the American Cancer Society and a grant, AM 03388, from the National Institute of Arthritis and Metabolic Diseases of the National Institutes of Health, United States Public Health Service.

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