colorless, and again with water. Removal of ether left 33 mg. of neutral steroid.

Attempted Michael Addition of Hydroquinone to 17β-Acetoxyandrost-1,4,6-trien-3-one.—A solution of $\Delta^{1,4,6}$-trienone (62 mg.) and 2,3-dichloro-5,6-dicyano-1,4-hydroquinone (90 mg.) in acetone (5 ml.) was allowed to stand for 10 min. Then ether was added, and the solution was washed with water, 2 *N* sodium hydroxide (three times), and finally with water. Removal of ether left unchanged $\Delta^{1,4,6}$-trienone (56 mg.).

Isolation of the Acidic By-product (VIII).—A stirred solution of 3-ethoxyandrost-3,5-dien-17-one (180 mg.) in acetone (6 ml.; dried over calcium chloride) was treated with a solution of DDQ (227 mg.) in acetone (1 ml.). The acetone was blown off by a rapid stream of nitrogen (10 min.), and the residue was suspended in benzene and filtered. The filtrate was diluted with ether and then washed successively with 0.2 *N* sodium hydroxide and water. Evaporation of the organic phase left 76 mg. of neutral steroid which was shown by thin layer chromatography to be a mixture of $\Delta^{4,6}$- and $\Delta^{1,4,6}$-3-keto steroids.

The alkali extracts were added to a saturated sodium chloride solution, and the resulting yellow gummy precipitate was separated by filtration. It was dissolved in methanol, diluted with water, and acidified with dilute sulfuric acid. Ether extraction gave a gum (67 mg.) which, after repeated crystallizations from ether and methanol–methylene chloride, gave VIII, m.p. 275–277°; ultraviolet spectrum showed $\lambda_{max}^{EtOH-HCl}$ 224 mμ (ε 23,500), 292 (19,400), shoulders 235 (20,500) and 345 (5100); $\lambda_{max}^{EtOH-NaOH}$ 210 mμ (ε 22,500), 254 (22,400), 285 (21,500), and 392 (6,700). The infrared spectrum showed bands at 4.51 (C≡N), 5.85 (17-ketone), 6.05 (3-ketone), and 6.20 μ (C=C); Beilstein test was positive.

Anal. Calcd. for $C_{27}H_{24}Cl_2N_2O_4$: C, 63.41; H, 4.73. Found: C, 63.64; H, 4.89.

Steroids. LXXI.[1,2] The Base-Catalyzed Reaction between Acetone and 20-Keto-16-pregnenes with 12β and 12α Substituents

MONROE E. WALL, F. I. CARROLL, AND G. S. ABERNETHY, JR.

Natural Products Laboratory, Research Triangle Institute, Durham, North Carolina

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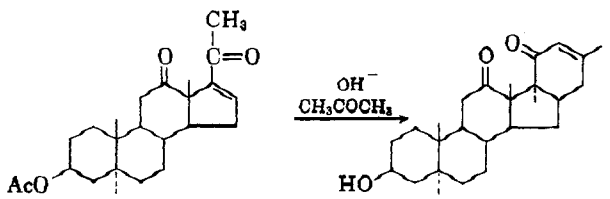
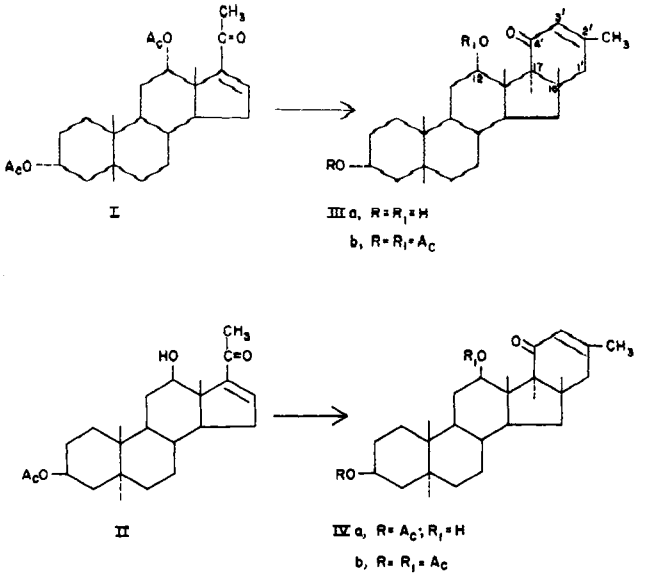
Reaction of 3α,12α-diacetoxy-5β-Δ^{16}-pregnen-20-one (I) or of 3β-acetoxy-12β-hydroxy-5α-Δ^{16}-pregnen-20-one (II) with acetone in the presence of potassium hydroxide gave the respective 16β,17α-cyclo derivatives (III and IV). The stereochemistry of these products are discussed in detail as are the hydrogen-bonding relationships between C-12 and C-20 or C-12 and C-4′ substituents.

Recently we established the structure and stereochemistry of the cyclic product formed by the base-catalyzed reaction of acetone with 3β-acetoxy-5α-Δ^{16}-pregnene-12,20-dione.[3] The reaction was shown to involve Michael addition followed by aldol condensation to give the pentacyclic product indicated below.



We now wish to report that the reactions of acetone with 3α,12α-diacetoxy-5β-Δ^{16}-pregnen-20-one (I) and with 3β-acetoxy-12β-hydroxy-5α-Δ^{16}-pregnen-20-one (II) give after acetylation the analogous cyclization products IIIb and IVa, respectively, although in much lower yield. To date we have been unable to demonstrate a similar reaction with 12-desoxy-16-dehydropregnenes.

The requisite 16-dehydropregnenes were made by slight modifications of literature procedures. The 12α-acetoxypregnene (I) was prepared *via* bromination of commercially available 3α,12α-diacetoxy-5β-pregnan-20-one, followed by treatment with sodium iodide and sodium metabisulfite.[4] The yield of pure I obtained by this procedure was poor (16.5%).[5] The preparation of the 12β-hydroxy-Δ^{16}-pregnene (II) involved slight modification of a preparation already in the literature.[6] Lithium aluminum hydride reduction of 3β-acetoxy-5α-Δ^{16}-pregnene-12,20-dione gave the crude triol, 3β,12β,20-trihydroxy-5α,Δ^{16}-pregnene. Selective oxidation of the allylic hydroxyl group with manganese di-



(1) Previous paper in this series, S. G. Levine, M. E. Wall, and N. H. Eudy, *J. Org. Chem.*, **28**, 1936 (1963).

(2) (a) The research reported in this paper was supported under contract SA-43-ph-4351 of the Cancer Chemotherapy National Service Center, National Cancer Institute, National Institutes of Health; (b) presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963.

(3) M. E. Wall, S. Serota, H. Kenney, and G. S. Abernethy, Jr., *J. Am. Chem. Soc.*, **85**, 1844 (1963).

(4) W. J. Adams, D. K. Patel, V. Petrow, and I. A. Stuart-Webb, *J. Chem. Soc.*, 1825 (1954).

(5) This reaction was studied briefly with the aid of thin layer chromatography. Bromination of 3α,12α-diacetoxy-5β-pregnan-20-one with 3 moles of bromine[4] gave a crude tribromo derivative which gave only one spot on thin layer chromatography (silica gel G). After treatment with sodium iodide and metabisulfite, a mixture of the initial pregnan-20-one and the desired Δ^{16}-pregnene (I) was obtained. The mixture was readily resolved on a thin layer chromatogram, and no tribromopregnene (this is much faster moving on t.l.c. than the pregnane or Δ^{16}-pregnene) was obtained.

(6) W. J. Adams, D. N. Kirk, D. K. Patel, V. Petrow, and I. A. Stuart-Webb, *J. Chem. Soc.*, 870 (1955).

oxide[7] followed by acetylation gave 3β-acetoxy-12β-hydroxy-5α-Δ16-pregnen-20-one (II), characterized by strong intramolecular hydrogen bonding of the 12β-hydroxyl group with the carbonyl group of the Δ16-20-ketone moiety,[8] as noted by the shift of the hydroxyl band to 3430 cm.$^{-1}$ and of the Δ16-20-ketone band to 1655 cm.$^{-1}$ from the normal positions, 3610 and 1665 cm.$^{-1}$, respectively.

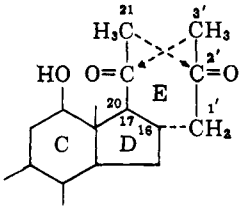
Treatment of the 12α-acetoxypregnene (I) with potassium hydroxide in aqueous acetone followed by room-temperature acetylation gave a new cyclization product, m.p. 214–215°, in 22% yield. The elemental analysis of this compound allows its formulation as the diacetoxy conjugated ketone (IIIb) by analogy with our results in the 12-ketone series.[3] The presence of a conjugated carbonyl group is shown by ultraviolet absorption ($\lambda_{max}^{CH_3OH}$ 235 mμ, ε 12,550) and by the presence of a strong band in the infrared at 1668 cm.$^{-1}$. The n.m.r. spectrum of IIIb displays a strong signal at 7.94 τ and a well defined weak signal at 4.44 τ, corresponding to signals at 7.98 and 4.23 τ found in the analogous 12-keto series[3] and attributed to the C-2′ methyl and C-3′ proton.

Starting instead with the 12β-hydroxy-Δ16-pregnene (II), the product from base-catalyzed condensation followed by acetylation is formulated on similar grounds as the corresponding pentacyclic derivative (IVa), m.p. 209–211°, $\lambda_{max}^{CH_3OH}$ 237 mμ (ε 12,300). Furthermore, the infrared spectrum of compound IVa revealed that the 12β-hydroxyl group was strongly hydrogen bonded to the C-4′ ketone[9] as indicated by the low frequency position of the conjugated carbonyl (1650 cm.$^{-1}$) and intense hydroxyl band (3390 cm.$^{-1}$). The correctness of this assignment was further proven by oxidation of IVa with chromium trioxide in acetone to give the known 12-ketone[3] (V). It is of interest that the non-bonded axial 12α-hydroxyl group in IIIa[10] is easily acetylated at room temperature, whereas the strongly hydrogen-bonded equatorial 12β-hydroxyl moiety in IVa cannot be acetylated under these conditions.[11] The data available does not permit a decision whether the observed difficulty in acetylation is due to strong intramolecular hydrogen bonding or to steric hindrance.

(7) F. Sondheimer, R. Amendolla, and G. Rosenkrantz, *J. Am. Chem. Soc.*, **75**, 5930 (1953).

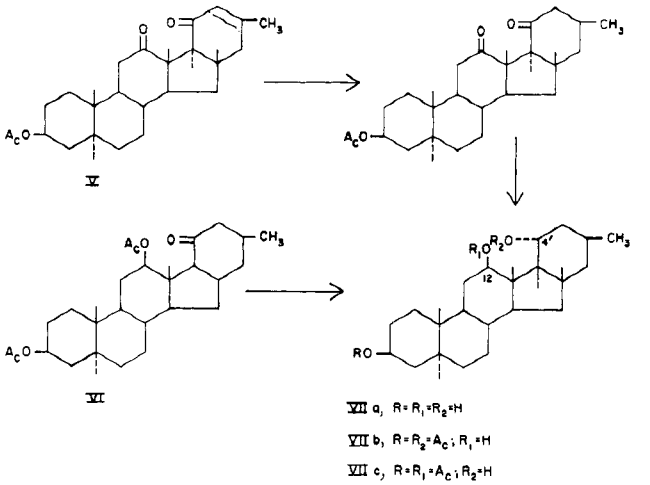
(8) M. E. Wall and S. Serota [*Tetrahedron*, **10**, 238 (1960)] have noted a similar case of intramolecular hydrogen bonding in the compound 3β-acetoxy-12β-hydroxy-12α-methoxy-5α,Δ16-pregnen-20-one.

(9) Theoretically, the hypothetical Michael adduct, which would initially be formed as the result of the base-catalyzed reaction of acetone with II, could cyclize *via* the aldol condensation in either of two directions as shown.



However, of the two possible products, only the compound with a carbonyl group in proximity to the 12β-hydroxyl moiety would be expected to display strong intramolecular hydrogen bonding.

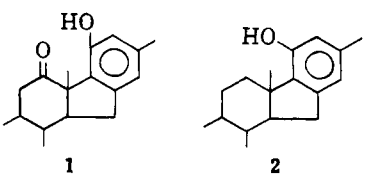
(10) This compound was not characterized but was undoubtedly formed as a result of the prolonged alkaline treatment at reflux temperature. The infrared spectrum (methylene chloride) showed strong hydroxyl absorption at 3600, weak nonbonded hydroxyl absorption at 3500–3300 cm.$^{-1}$, and the absence of acetate carbonyl absorption. Acetylation yielded crystalline IIIb.



Perchloric acid-catalyzed acetylation of IVa gave the diacetate (IVb) which showed an ultraviolet maximum at 234 mμ (ε 12,500), the corresponding infrared band appearing at 1680 cm.$^{-1}$. The conjugated double bond of IVb was smoothly hydrogenated in the presence of 5% palladium on charcoal yielding the saturated diacetate (VI). Reduction of VI at 25° with lithium aluminum (tri-*t*-butoxy) hydride gave a hydroxy diacetate which was very soluble in all common solvents and could not be crystallized. After purification by preparative thin layer chromatography, the product VIIc was shown to be pure by analytical thin layer chromatography in several solvent systems and gave a satisfactory elemental analysis. The infrared spectrum of VIIc indicated that the C-4′ hydroxyl moiety was strongly hydrogen bonded to the *ether oxygen* of the 12β-acetate group as noted by the presence of an intense, narrow width band at 3575, a partially resolved broad band 1735–1750 (3β-acetate, 1735; 12β-acetate, 1750), and a split band 1240 and 1220 cm.$^{-1}$ (asymmetric C–O–C stretching band of 3β- and 12β-acetate groups, respectively). Henbest and Lovell[12] have discussed this type of hydrogen bonding in detail[13]; *cf.* also ref. 3. The n.m.r. spectrum of VIIc exhibited a strong signal at 9.18 τ (C-18 and C-19 methyl groups), a doublet at 9.04 and 9.13 τ (J = 5.4 c.p.s., methyl group attached to C-2′ carbon atom), and broad, weak peaks centered at approximately 5.5, 6.4, and 7.3 τ attributed, respectively, to the combined C-3 α- and C-12 α-axial protons, the C-4′ β-axial proton, and the proton of the C-4′ α-hydroxyl group.[14]

The evidence previously cited permits clarification of most of the stereochemical features of ring E in compound VIIc. The ring D/E fusion is 16βH, 17αH,

(11) Similarly the 12β-hydroxyl group of the hydrogen-bonded pregnene (II) could not be acetylated. Indeed the phenomenon seems quite general. Of the two cyclic phenols **1** and **2**, *cf.* ref. 3, phenol **1** is strongly hydrogen



1 **2**

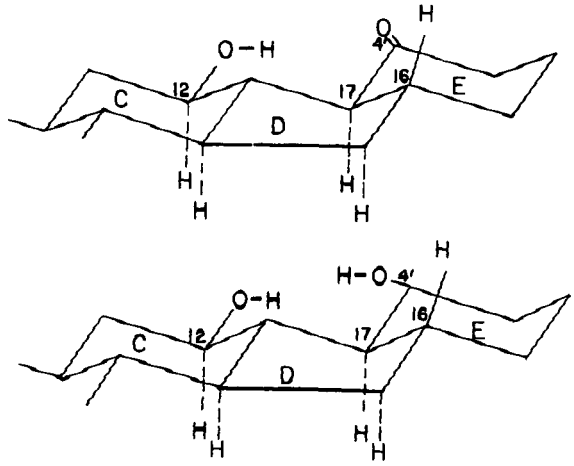
bonded to the C-12 ketone and cannot be acetylated under mild conditions. Compound **2** lacks the C-12 ketone and hence is not intramolecularly hydrogen bonded. It is easily acetylated under mild conditions.

(12) H. B. Henbest and B. J. Lovell, *J. Chem. Soc.*, 1965 (1957).

(13) Ref. 3, footnote 16, and text to which footnote refers.

(14) J. N. Shoolery and M. T. Rogers, *J. Am. Chem. Soc.*, **80**, 5121 (1958).

since the precursor of VIIc, compound IVa, was shown to have this ring fusion by oxidation to the known 12-keto derivative (V).[3] Dreiding and Courtauld molecular models constructed on the reasonable assumption that ring E would be in all chair form indicate that of the two possible C-4′ hydroxyl isomers only the epimer with the 4α configuration could exhibit the intramolecular hydrogen bonding previously discussed. In a compound with this structure the proton attached to C-4′ should have the axial conformation, and, as we have shown, the n.m.r. spectrum of VIIc does indeed show the presence of such a proton. Still awaiting clarification is the stereochemistry of the methyl group attached to the C-2′, a subject which is under study.



Previously we reported the preparation of a crystalline monohydroxydiacetate with the same empirical formula as VIIc[15] (*cf.* ref. 3, compound IXa, and footnote 16). One acetoxyl group could be located at C-3 but the choice between C-12 or C-4′ for the other was not clear-cut. Alkaline hydrolysis of VIIc gave triol VIIa which was not characterized other than by infrared spectrum. Mild acetylation of VIIa gave VIIb, a crystalline compound which proved to be identical with the previously described compound of uncertain structure.[3,15] The compounds VIIb and VIIc differed also in their infrared spectra in the region 1050–900 cm.$^{-1}$.[16] On the other hand intramolecular hydrogen bonding was noted in the case of VIIb and was similar to that previously described for VIIc. In view of these results, VIIc and VIIb most likely differ only in the juxtaposition of the acetoxyl and hydroxyl groups at C-12 and C-4′, the former being assigned the 12β-acetoxy-4′α-hydroxy and the latter the 12β-hydroxy-4′α-acetoxy structure. On the basis of molecular models, the C-4′ α-hydroxyl group appears less hindered than the 12β-hydroxyl, and hence it is not surprising that it is preferentially acetylated. We have aleady noted that hydroxyl groups in this general series which are intramolecularly hydrogen bonded to ketones cannot be acetylated under mild conditions.

Experimental[17]

3β-Acetoxy-12β-hydroxy-5α,16-pregnen-20-one (II).—The above compound was prepared according to the method of Adams, Kirk, Patel, Petrow, and Stuart-Webb[6] using the following modified procedure. To a stirred refluxing suspension–solution of 4 g. (0.105 mole) of crushed lithium aluminum hydride in 300 ml. of tetrahydrofuran (distilled from lithium aluminum hydride) was added 22.5 g. (0.0605 mole) of 3β-acetoxy-5α,16-pregnen-12,-20-dione dissolved in 500 ml. of dry tetrahydrofuran. The reaction mixture was allowed to reflux for 2 hr. more after the addition. The excess lithium aluminum hydride was decomposed with water and 150 g. of solid anhydrous sodium sulfate was added. The solids were removed by filtration and washed well with tetrahydrofuran. The washings were added to the filtrate. Removal of the tetrahydrofuran under reduced pressure followed by drying in the vacuum oven afforded 20.2 g. (100%) of crude 3β,12β,20-trihydroxy-5α,16-pregnene. The infrared spectrum showed strong peaks at 3600 and 3400 cm.$^{-1}$ and showed no adsorption in the carbonyl region. The crude 3β,12β,20-trihydroxy-5α-16-pregnene was dissolved in 2 l. of chloroform and refluxed 4 hr. with 102 g. of manganese dioxide. The cooled filtered solution was taken to dryness, and the residue was acetylated with acetic anhydride–pyridine at room temperature overnight to afford 19.5 g. of crude product which was chromatographed on 200 g. of Florisil using benzene as solvent.

Elution with benzene and benzene–methylene chloride afforded a solid which, on crystallization from isopropyl alcohol, yielded 8.35 g. (37%) of crystals, m.p. 216–220°, lit.[6] m.p. 222–224°, $\lambda_{max}^{CH_3OH}$ 242 mμ (ε 8,800); the infrared spectrum shows a strong bonded hydroxyl adsorption at 3430 and a strong carbonyl peak at 1655 cm.$^{-1}$.

3β-Acetoxy-12β-hydroxy-2′-methyl-5α,16β,17α-(16,17-butanoandrost-2′-en)-4′-one (IVa).[18]—A stirred mixture of 5.7 g. (15.2 mmoles) of 3β-acetoxy-12β-hydroxy-5α,16-pregnen-20-one, 85.5 ml. of acetone, 8.6 g. of potassium hydroxide, and 52 ml. of water were refluxed together for 5 hr. The acetone solution was concentrated under reduced pressure, and the remaining residue was diluted with water, extracted with ether, and dried over magnesium sulfate. Concentration of the ether afforded 5.17 g. of crude product which was acetylated with acetic anhydride–pyridine at room temperature overnight. After the usual work-up, the crude product was dissolved in ether and was cooled to afford 0.98 g. (15.5%) of II, m.p. 200–209°. The filtrate was concentrated, dissolved in benzene, and chromatographed on 300 g. of Florisil. A 1.30-g. fraction eluted with benzene–2% methanol was recrystallized from methanol to yield an additional 0.6 g. (9.5%) of II, m.p. 202–210°. The analytical sample was recrystallized from methanol, m.p. 209–211°, $[\alpha]^{24}D$ +105.8°, $\lambda_{max}^{CH_3OH}$ 237 mμ (ε 12,286); the infrared spectrum (methylene chloride) showed a strong bonded hydroxyl peak at 3390, acetate peak at 1720, conjugated carbonyl peak at 1650, and a double bond peak at 1612 cm.$^{-1}$.

Anal. Calcd. for $C_{26}H_{38}O_4$: C, 75.32; H, 9.23. Found: C, 75.07; H, 9.13.

3β,12β-Diacetoxy-2′-methyl-5α,16β,17α-(16,17-butanoandrost-2′-en)-4′-one (IVb).—To a solution of 0.65 g. (0.00157 mole) of butanoandrostene (IVa) in 6.5 ml. acetic acid and 2.0 ml. acetic anhydride at 18° was added 0.06 ml. of 5 *N* perchloric acid. The resulting solution was stirred at 20° for 1 hr. and was poured into an ice–water slurry. The suspension was extracted with ether and the extracts were washed with water and bicarbonate solution. After drying over magnesium sulfate, evaporation of the extracts yielded 0.70 g. of colorless glass. The infrared spectrum shows no –OH band. Crystallization from heptane afforded 0.525 g. of crystals, m.p. 160–163°; the analytical sample crystallized from heptane, m.p. 163–165°, $[\alpha]^{25}D$ +135°, $\lambda_{max}^{CH_3OH}$ 234 mμ (ε 12,500). The infrared spectrum showed a broad ester band at 1725–1735 (3β,12β-acetates) and a weaker band at 1680 cm.$^{-1}$ ($\Delta^{2'}$-4′-ketone).

Anal. Calcd. for $C_{28}H_{40}O_5$: C, 73.65; H, 8.83. Found: C, 73.99; H, 8.88.

3β-Acetoxy-2′-methyl-5α,16β,17α-(16,17-butanoandrost-2′-ene)-4′,12-dione (V).—To a stirred solution of 0.197 g. (4.75 mmoles) of IVa in 20 ml. of acetone (distilled from potassium permanganate) was added 0.138 ml. of standard chromate re-

(15) The route involved catalytic reduction of the $\Delta^{2'}$-4′,12-diketone (V) followed by reduction with lithium in liquid ammonia or lithium aluminum hydride and acetylation of the resultant 3,12,4′-triol with acetic anhydride in pyridine at room temperature.

(16) VIIb shows strong bands at 1030, 950, and 910 cm.$^{-1}$; VIIc possesses strong bands at 1045, 1025, 970, and 910 cm.$^{-1}$.

(17) Unless otherwise noted, all melting points were obtained on the Kofler hot stage, optical rotations in chloroform solution, ultraviolet spectra in methanol, infrared spectra in carbon disulfide or methylene chloride, and n.m.r. spectra in deuteriochloroform solution using a Varian spectrometer operating at 60 Mc. and calibrated against internal tetramethylsilane.

(18) The nomenclature adopted was recommended by *Chemical Abstracts*, *cf.* ref. 3, footnote 26.

agent.[19] Nitrogen was bubbled through the reaction mixture. After 1 hr. at room temperature, the chromate color had disappeared and 0.2 ml. more of standard chromate reagent was added. After 1 hr. the excess chromate was decomposed with aqueous sodium metabisulfite. The reaction mixture was diluted with water and was extracted with methylene chloride. The extracts were washed with dilute potassium hydroxide and with water and were dried over magnesium sulfate. Removal of the methylene chloride and drying afforded 0.196 g. of a foam. Crystallization from methanol yielded 0.120 g. (61.3%) of V, m.p. 238–240°, lit.[3] m.p. 243–246°. The infrared spectrum of V was identical with the spectrum of an authentic sample.[3]

3α,12α-Diacetoxy-5β,16-pregnen-20-one (I).—3α,12α-Diacetoxy-5β-Δ[16]-pregnen-20-one was prepared according to the method reported by Adams, Patel, Petrow, and Stuart-Webb.[4] From 25 g. (0.0598 mole) of 3α,12α-diacetoxy-5β-pregnan-20-one, 4.1 g. (16.5%) of I was obtained, m.p. 198–199°, lit.[4] m.p. 190–192°.

3α,12α-Diacetoxy-2′-methyl-5β,16β,17α-(16,17-butanoandrost-2′-en)-4′-one (IIIb).—This reaction was conducted in the same manner as described for the preparation of IVa using 4.0 g. (9.6 mmoles) of 3α,12α-diacetoxy-5β,16-pregnen-20-one, 60 ml. of acetone, 38 ml. of water, and 6 g. of potassium hydroxide. The crude product was acetylated with acetic anhydride–pyridine at room temperature overnight. The usual work-up afforded 4.08 g. of a foam which was dissolved in benzene and chromatographed on 200 g. of Florisil. A fraction weighing 1.32 g. was eluted with benzene–2% methanol. Recrystallization from cyclohexane yielded 0.98 g. (22.4%) of IIIb, m.p. 213.5–214.5°. The analytical sample was recrystallized from isopropyl alcohol, m.p. 214–215°, $[\alpha]^{24}D$ +122°, $\lambda_{max}^{CH_3OH}$ 235 mμ (ε 12,550); the infrared spectrum (methylene chloride) showed the presence of a strong band at 1720 (acetate carbonyl), conjugated ketone carbonyl peak at 1668, and a double bond peak at 1612 cm.$^{-1}$.

Anal. Calcd. for $C_{28}H_{40}O_5$: C, 73.65; H, 8.83. Found: C, 73.35; H, 8.75.

3β,12β-Diacetoxy-2′-methyl-5α,16β,17α-(16,17-butanoandrostan)-4′-one (VI).—To a solution of 0.525 g. (0.00157 mole) of the diacetate (IVb) in 50 ml. of methanol was added 0.25 g. of 5% palladium-on-carbon catalyst. The mixture was hydrogenated for 1 hr. at room temperature with stirring. The catalyst was filtered off, and the filtrate was evaporated to dryness *in vacuo* yielding 0.50 g. of colorless glass. Crystallization from petroleum ether afforded 0.30 g. of crystals that had m.p. 148–149.5°. The analytical sample crystallized from petroleum ether, m.p. 150–151°, $[\alpha]^{24}D$ +37°; the infrared spectrum (carbon disulfide) shows a peak at 1730–1735 (3β,12β-acetate carbonyls) and 1719 cm.$^{-1}$ (4′ ketone).

Anal. Calcd. for $C_{28}H_{42}O_5$: C, 73.32; H, 9.23. Found: C, 73.02; H, 9.28.

3β,12β-Diacetoxy-2′-methyl-5α,16β,17α-(16,17-butanoandrostan)-4′α-ol (VIIc).—To 0.25 g. of VI (0.005 mole) in 10 ml. of dry tetrahydrofuran was added 1.0 g. of lithium aluminum tri-*t*-butoxy hydride. The solution was allowed to stand overnight at room temperature. Aqueous acetic acid was added and the tetrahydrofuran removed *in vacuo* at room temperature. The residual suspension was extracted with ether and the extracts were washed with bicarbonate solution until neutral. After drying, the extracts were evaporated to dryness yielding 0.24 g. of a glass. Preparative thin layer chromatography on silica gel G (1:1:1 benzene–ethyl acetate–chloroform eluent) afforded 0.190 g. of colorless glass which was shown to be pure by analytical thin layer chromatography using three solvent systems: (a) 1:1:1 benzene–ethyl acetate–chloroform, R_f 0.69; (b) 3% isopropyl alcohol in benzene, R_f 0.32; (c) 15% acetone in petroleum ether, R_f 0.43. This material could not be obtained in crystalline form. An analytical sample was prepared by dissolving the glass in a small volume of benzene, freeze-drying, and drying the residual foam *in vacuo* over refluxing ethanol in an Abderhalden dryer. The infrared spectrum shows a strong hydroxyl band at 3575, a broad carbonyl band at 1730–1750, and C–O stretching bands at 1240 and 1220 cm.$^{-1}$; $[\alpha]^{24}D$ −70°.

Anal. Calcd. for $C_{28}H_{44}O_5$: C, 73.00; H, 9.63. Found: C, 73.07; H, 9.74.

2′-Methyl-5α,16β,17α-(16,17-butanoandrostane)-3β,12β,4′α-triol (VIIa).—A solution of the monohydroxy diacetate (VIIc, 0.140 g.) in 10 ml. of 10% methanolic potassium hydroxide was heated on a steam bath for 1 hr. After removal of the methanol *in vacuo*, water was added, and the resulting suspension was extracted with ether. On drying and evaporation to dryness, 0.126 g. of crystalline solid was obtained. The infrared spectrum shows no carbonyl band.

3β,4α-Diacetoxy-2′-methyl-5α,16β,17α-(16,17-butanoandrostan)-12β-ol.—Triol VIIa (0.1 g.) was dissolved in 2 ml. of acetic anhydride and 2 ml. of pyridine and allowed to stand at 25° overnight. The liquid was removed *in vacuo* yielding a mixture of crystals and glass. Trituration with methanol afforded 0.078 g. of crystals, m.p. 203–206°. The infrared spectrum was identical with that of a compound previously prepared.[3,15] The melting point of this compound was 205–207°. A mixture of this compound and an authentic sample of VIIb[3] melted at 203–207°.

(19) A solution of 26.72 g. of chromium trioxide in 23 ml. of concentrated sulfuric acid diluted with water to a volume of 100 ml. was used.

A Tautomeric Nitrile–Thiol Iminothiolactone System[1]

GARDNER W. STACY, ANTHONY J. PAPA,[2] F. WARREN VILLAESCUSA, AND SUVAS C. RAY

Department of Chemistry, Washington State University, Pullman, Washington

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An interesting type of ring-chain tautomerism has been studied. When Ia,b was reduced with sodium borohydride–aluminum chloride (3:1), its tautomeric character became apparent in that products corresponding to both the chain form, (1-aminomethyl-2-naphthyl)methanethiol (II, 17%), and ring form, 1,3-dihydronaphtho[1,2-*c*]thiophene (III, 48%), resulted. It was found that when the proportion of sodium borohydride–aluminum chloride was increased from 3:1 to 4:1, II was obtained as the sole product (51%). The structure of I in the solid state and in chloroform solution appears to be that of naphtho[1,2-*c*]thiophen-1(3*H*)-imine (Ib) as confirmed by infrared and n.m.r. spectra. The chemical properties of I under neutral and acidic reaction conditions also substantiate this structure (Ib). In agreement with the conditions of reduction, in basic media it is possible to demonstrate the chain tautomeric structure (Ia) by sulfide and disulfide formation.

Reduction of the substance Ia,b with sodium borohydride–aluminum chloride (3:1) resulted in a demonstration of its tautomeric character by the formation of (1-aminomethyl-2-naphthyl)methanethiol (II), and 1,3-dihydronaphtho[1,2-*c*]thiophene (III). The structure of II was confirmed by conversion to the amino disulfide, which subsequently was acetylated to a diacetyl compound. Structure III, a new sulfur heterocyclic system, was established simply by Raney nickel desulfurization to 1,2-dimethylnaphthalene. The hydrogenolysis by sodium borohydride of the imino group of Ib to form III may occur by the mechanism pro-

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