Anal. Calcd. for $C_{10}H_{14}N_2O_2 \cdot 2C_6H_3N_3O_7$: C, 41.5; H, 3.2; N, 17.6. Found: C, 41.6; H, 3.0; N, 17.7.

It should be pointed out that neither II, III, nor IV can be satisfactorily extracted from aqueous solution with organic solvents.

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Addition of Alkanethiolic Acids to $\Delta^{1,4,6}$-3-Oxosteroids

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Recently some selective additions to $\Delta^{1,4,6}$-3-oxosteroids have been reported. Nussbaum and coworkers[1] have reported the epoxidation of the 6,7-double bond, and Kirk and Petrow[2] recorded the addition of chlorine to the 1,2-double bond. We have observed mono- and di- additions of alkanethiolic acids to the $\Delta^{1,4,6}$-3-ketones. When 1,4,6-androstatriene-3,17-dione was heated with ethanethiolic acid, a monoadduct separated rapidly from the hot solution. The same product was obtained from a chloroform solution of equimolar amounts of triene and thiolic acid irradiated with an ultraviolet lamp. On the basis of its ultraviolet spectrum ($\lambda_{\max}^{\text{methanol}}$ 287 mμ, ϵ 23,400) and of analogy to the addition of thiolic acids to $\Delta^{1,4}$-3-oxosteroids,[3] this product was assigned the structure, 1α-acetylthio-4,6-androstadiene-3,17-dione.

In the cases of 17β-acetoxy-1,4,6-androstatrien-3-one, 17α,21-dihydroxy-1,4,6-pregnatriene-3,11,20-trione 21-acetate, and 11β,17α,21-trihydroxy-1,4,6-pregnatriene-3,20-dione 21-acetate, the products isolated were di-adducts (exhibiting maxima in the 240 mμ region characteristic of Δ^4-3-ketones). Again by analogy to monoadditions,[3] these compounds were assigned the 1α,7α-diacylthio structures.

EXPERIMENTAL[4]

1α-Acetylthio-4,6-androstadiene-3,17-dione. 1,4,6-Androstatriene-3,17-dione,[5] 2.00 g., was dissolved in 5.0 ml. of ethanethiolic acid and irradiated and heated with an ultraviolet light for 1 hr. During this time crystals formed. They were separated by filtration, washed with ether, and crystallized from methylene chloride-methanol. In this way 1.00 g. of 1α-acetylthio-4,6-androstadiene-3,17-dione, m.p. 229–229.5° (dec.), was obtained.

Anal. Calcd. for $C_{21}H_{26}O_3S$: C, 70.36; H, 7.31. Found: C, 70.38; H, 7.33. Ultraviolet spectrum: $\lambda_{\max}^{\text{methanol}}$ 287 mμ, ϵ 23,400. $[\alpha]_D$ +68°.

1α,7α-Dithiol-11β,17α,21-trihydroxy-4-pregnene-3,20-dione 21-acetate 1,7-dipropionate. 11β,17α,21-Trihydroxy-1,4,6-pregnatriene-3,20-dione 21-acetate,[6] 0.87 g., dissolved in 1.0 ml. of propanethiolic acid, was heated on the steam bath for several hours. Most of the excess thiolic acid was removed under vacuum and the residue was chromatographed on silica gel. The column was washed with benzene and mixtures of 5 and 10% ethyl acetate in benzene. Then the column was eluted with 15% ethyl acetate in benzene and the eluants were concentrated to yield 0.20 g. of 1α,7α-dithiol-11β,17α,21-trihydroxy-4-pregnene-3,20-dione 21-acetate 1,7-dipropionate as a glass.

Anal: Calcd. for $C_{29}H_{40}O_8S_2$: C, 59.97; H, 6.94. Found: C, 59.91; H, 7.05. Ultraviolet spectrum $\lambda_{\max}^{\text{methanol}}$ 239 mμ, ϵ 21,200; $[\alpha]_D$ +37°.

1α,7α-Dithiol-17β-hydroxy-4-androsten-3-one triacetate. 17β-Acetoxy-1,4,6-androstatrien-3-one,[5] 1.93 g., was mixed with 2.0 ml. of ethanethiolic acid and heated and irradiated with an ultraviolet light for 45 min. Some of the excess thiolic acid was distilled under vacuum, ether was added to the residue, and the solid which formed was separated by filtration. Two crystallizations of this material from acetone-ether yielded 0.91 g. of 1α,7α-dithiol-17β-hydroxy-4-androsten-3-one triacetate, m.p. 199–200° (dec.).

Anal. Calcd. for $C_{25}H_{34}O_5S_2$: C, 62.73; H, 7.16. Found: C, 62.68; H, 7.46. Ultraviolet spectrum: $\lambda_{\max}^{\text{methanol}}$ 237.5 mμ, ϵ 20,100; $[\alpha]_D$ −46°.

1α,7α-Dithiol-17α,21-dihydroxy-4-pregnene-3,11,20-trione 1,7,21-triacetate. 17α,21-Dihydroxy-1,4,6-pregnatriene-3,11,-20-trione 21-acetate,[6] 0.54 g., was dissolved in 1.0 ml. of ethanethiolic acid and heated and irradiated with an ultraviolet light for 1 hr. Then part of the excess acid was removed under vacuum and ether was added. The solid which formed was separated by filtration and crystallized from acetone-ether to yield 0.38 g. of 1α,7α-dithiol-17α,21-dihydroxy-4-pregnene-3,11,20-trione 1,7,21-triacetate, m.p. 190–191° (dec.).

Anal. Calcd. for $C_{27}H_{34}O_8S_2$: C, 58.89; H, 6.22. Found: C, 59.05; 58.72; H, 6.70, 6.53. Ultraviolet spectrum: $\lambda_{\max}^{\text{methanol}}$ 235.5 mμ, ϵ 18,500; $[\alpha]_D$ +80°.

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[4] We wish to thank Dr. R. T. Dillon and his staff of the Analytical Division for the microanalyses and optical determinations reported. The rotations were taken in chloroform at 24 ± 1°. The melting points were taken on a Fisher-Johns melting point apparatus.

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Synthesis of 1,2,4,5-Tetrachlorobenzene-1-Cl^{36}

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1,2,4,5-Tetrachlorobenzene has been under investigation in this laboratory for use as an agricultural chemical. The compound, labeled with chlorine-36, was desired for residue determinations using an isotope dilution procedure. Since it had not previously been prepared the synthesis was undertaken employing the Sandmeyer reaction.