anhydride with *o*-phenylenediamine at 200° and purifying the crude product by crystallization from acetic acid.

**Benzimidazo[1,2-*b*]isoquinoline-5,12-dione from II.**—A solution of *p*-nitroso-N,N-dimethylaniline hydrochloride (0.33 g) in methanol (12 ml) was made alkaline (pH 8.5) by adding a 2 *N* solution of sodium hydroxide at 5°. Benzimidazo[1,2-*b*]isoquinolin-5(12H)-one (II, 0.55 g) dissolved in dimethylformamide (30 ml) was then added, and the mixture was stirred at room temperature for 10–15 min. The addition of water (50 ml) precipitated the *p*-dimethylaminophenylimino derivative of II (0.35 g) as violet needles, mp 236–238°.

*Anal.* Calcd for $C_{23}H_{18}N_4O$: C, 75.2; H, 4.9; N, 15.3. Found: C, 75.2; H, 4.9; N, 15.3.

To a slurry of the above *p*-dimethylaminophenylimino derivative (5 g) in acetic acid (125 ml) a 2 *N* solution of hydrochloric acid (20 ml) was added dropwise. After stirring at room temperature for 30 min, water (125 ml) was added, and the stirring was continued for an additional 10 min. The collected dull reddish precipitate (2.5 g) crystallized from acetic acid in the presence of a small amount of chromic acid gave 2 g of benzimidazo-[1,2-*b*]isoquinoline-5,12-dione of mp 267–269°. The infrared spectrum shows a strong carbonyl band at 5.86 and a carboxamide band at 5.98 $\mu$.

*Anal.* Calcd for $C_{15}H_8N_2O_2$: C, 72.4; H, 3.2; N, 11.2. Found: C, 72.3; H, 3.1; N, 11.2.

**Proof of Structure of Benzimidazo[1,2-*b*]isoquinoline-5,12-dione Obtained from II. 2-(*o*-Methylbenzyl)benzimidazole.**—A stirred suspension of *o*-tolylacetic acid (21 g) and *o*-phenylenediamine (10.8 g) in 4 *N* hydrochloric acid (100 ml) brought to reflux over a 30-min period was boiled for 24 hr and then allowed to cool to room temperature. The collected precipitate was slurried in water (200 ml), made alkaline with sodium carbonate solution, and stirred for an additional hour. The filtered product recrystallized from ethanol gave white crystals (50% yield), mp 220–221°.

*Anal.* Calcd for $C_{15}H_{14}N_2$: C, 81.0; H, 6.3; N, 12.6. Found: C, 81.0; H, 6.3; N, 12.2.

**Benzimidazo[1,2-*b*]isoquinoline-5,12-dione (V).**—Chromic acid (6 g) was added in portions to a solution of 2-(*o*-methylbenzyl)-benzimidazole (2.1 g) in acetic acid (20 ml), maintained at 70°, and the mixture was stirred at this temperature for 20 hr. The precipitate obtained by pouring the reaction mixture into water and stirring for about 0.5 hr was collected, boiled with ethanol for 15 min, and filtered hot. Crystallization from acetic acid gave V as shiny, pale yellow plates (yield 30%) of mp 267–269°.

*Anal.* Calcd for $C_{15}H_8N_2O_2$: C, 72.4; H, 3.2; N, 11.2. Found: C, 72.3; H, 3.2; N, 11.1.

A mixture of V with the dione obtained from II (mp 267–269°) melted at 267–269°. The identity of the two diones of mp 267–269° was further substantiated by comparison of the infrared spectra.

**12,12′-Ethanediylidenebisbenzimidazo[1,2-*b*]isoquinolin-5-(12H)-one (VI).**—Eleven grams of glyoxal sulfate was added to a mixture of 24 g of benzimidazoisoquinolinone (II) in 200 ml of dimethylformamide. The temperature rapidly rose 10–15° and a thick precipitate of dark red needles began to form. The suspension was warmed to 80° and filtered hot. The precipitate washed with dimethylformamide and with alcohol and dried gave 22 g (87% yield) of VI, as red needles. VI is insoluble in all common organic solvents. It dissolves readily in sulfuric acid to give a blood red solution.

**Bisbenzimidazo[1,2-*b*:1′,2′-*b*′]pentaleno[1,2,3-*d*,*e*:4,5,6-*d*′,*e*′]-diisoquinoline-9,19-dione (VII).**—An intimate mixture of 25 g of VI and 25 g of sodium *m*-nitrobenzenesulfonate (Sitol) was added in small portions to a melt of 250 g of aluminum chloride, 65 g of sodium chloride, and 25 g of sodium *m*-nitrobenzenesulfonate held at 120–130°. One-half hour after the addition was complete, the hot mixture was drowned in 1500 ml of ice and water and then filtered. The moist cake was redissolved in 110 ml of sulfuric acid and reprecipitated into 200 ml of water. Sodium dichromate (50 g) was added, and the mixture was heated for 0.5 hr at 60–80°. The collected precipitate washed with water and with alcohol gave 12 g of VII, as a reddish violet solid. VII was purified by dissolving it in about 10 times its weight of concentrated sulfuric acid and then slowly diluting with cooling to a concentration of 85–90% sulfuric acid.

**12-(2,2-Dichloroethylidene)benzimidazo[1,2-*b*]isoquinolin-5-(12H)-one (VIII).**—Benzimidazoisoquinolinone II (120 g) was added slowly to a mixture of 1500 ml of dimethylformamide and 175 ml of freshly distilled dichloroacetaldehyde, while stirring at 45–50°. A thick mass of transparent needles formed. After 1 hr at 45–50°, the product was filtered and washed with alcohol to give 124 g of VIII. This product could not be recrystallized satisfactorily since it decomposed at elevated temperatures.

*Anal.* Calcd for $C_{17}H_{10}Cl_2N_2O$: Cl, 21.2; N, 8.4. Found: Cl, 21.6; N, 8.4.

**12-(10-Oxo-9-anthrylideneethylidene)benzimidazo[1,2-*b*]isoquinolin-5(12H)-one (IX).**—(Dichloroethylidene)benzimidazoisoquinolinone (VIII, 3.3 g) was dissolved in 25 ml of sulfuric acid to give a bright red solution. Anthrone (1.8 g) was then added, and the mixture was warmed to 40–50°. The solution became much bluer and hydrochloric acid was evolved. After 0.5 hr the filtered product was washed acid-free to give 3.6 g of IX as brown powder.

*Anal.* Calcd for $C_{31}H_{18}N_2O_2$: N, 6.2. Found: N, 6.3.

The product was recrystallized by carefully diluting a solution in sulfuric acid with water.

**Anthra[9,1-*a*,*b*]pentaleno[4,5,6-*d*,*e*]benzimidazo[1,2-*b*]isoquinoline-8,18-dione (X).**—A mixture of 1 g of IX and 1 g of sodium *m*-nitrobenzenesulfonate was added to a melt of 20 g of aluminum chloride, 5 g of sodium chloride, and 1 g of sodium *m*-nitrobenzenesulfonate maintained at 120–130°. After 0.5 hr at this temperature, the mixture was precipitated into a slurry of 150 ml of ice and 15 ml of hydrochloric acid. The filtered precipitate was washed acid-free to give 0.4 g of X as a dark brown powder.

# Synthesis and Reactions of 17β-Acetoxy-5α-androstan-3-yl Isocyanates

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17β-Acetoxy-5α-androstan-3α-yl isocyanate (IIIc) and 17β-acetoxy-5α-androstan-3β-yl isocyanate (IVc) were synthesized by the action of phosgene on the corresponding amines. The isocyanates react characteristically with ethanol, mercaptans, and amines to give carbamates, thiocarbamates, and ureas, respectively. Cysteine reacts preferentially at the thiol group.

Recent publication of the preparation of 3α-iodo-2β-cholestanyl isocyanate[1] prompts us to report our own work on the synthesis and reactions of two steroidal isocyanates.[2] Sodium borohydride reduction of 17β-acetoxy-5α-androstan-3-one gave a mixture of epimers predominating in the 3β-ol. Treating the mixture with methanesulfonyl chloride, according to Chang,[3] afforded a mixture of mesylates I and II that was separated by fractional crystallization (Scheme I). Individually the mesylates reacted with sodium azide in dimethyl sulfoxide[4] to give azides IIIa and IVa, which

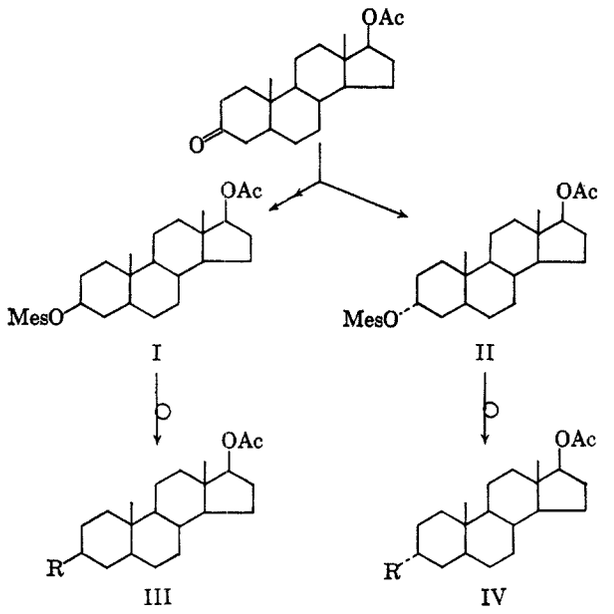
(1) A. Hassner and C. Heathcock, *J. Org. Chem.*, **30**, 1748 (1965).

(2) Steroidal isocyanates have been prepared as intermediates, which were not characterized: I. G. Farbenind., British Patent 465,960 (1937); French Patent 819,975 (1937); Swiss Patent 225,781 (1943).

(3) F. C. Chang, *J. Chinese Chem. Soc.* (Taiwan), **9**, 53 (1962).

(4) K. Ponsold, *J. Prakt. Chem.*, **25**, 32 (1964).

SCHEME I




IIIa, R = $N_3$–
b, R = $NH_2$–
c, R = OCN–
d, R = $C_2H_5SCONH$–
e, R = $(n\text{-}C_4H_9)_2NCONH$–
f, R = $H_3{}^+NCH(CO_2{}^-)CH_2SCONH$–
g, R = $C_2H_5OCOCH_2SCONH$–
h, R = $C_2H_5OCOCH_2NHCONH$–

IVa, R = $N_3$–
b, R = $NH_2$–
c, R = OCN–
d, R = $CH_3CONH$–
e, R = $C_2H_5OCOCH_2SCONH$–

were reduced with hydrazine and Raney nickel[4] to give amines IIIb and IVb. The action of phosgene on these amines[5] gave the corresponding isocyanates IIIc and IVc. 17β-Acetoxy-5α-androstan-3α-yl isocyanate (IIIc) underwent the expected reactions with ethanol, ethanethiol, and di-*n*-butylamine to give the corresponding carbamate, thiocarbamate, and urea, respectively. Analogous reactions occurred with cysteine,[6] ethyl mercaptoacetate, and ethyl glycinate, as evidenced by infrared spectra of the products (IIIf, g, and h).

Theoretically the isocyanate could attack cysteine at either the sulfur or the nitrogen. The infrared spectrum of IIIf is indicative of the thiocarbamate, rather than urea structure, but a broad absorption at 6.1–6.2 μ ($-CO_2^-$) obscures this region. The presence of a free amino group, thus requiring the thiocarbamate structure, was shown conclusively by preparation of the hydrochloride, with concomitant changes in the infrared spectrum as expected [*e.g.*, the 6.1–6.2-μ band was replaced by a 5.77-μ ($CO_2H$) band, which coincides with the 17-acetate band].

Configuration in the α series is indicated by reaction of IIIc with ethanol to give the known N-carbethoxy derivative,[7] and in the β series by conversion of IVb to the corresponding acetamide IVd.[8] Assuming inversion of configuration during azidolysis,[9] I and II are assigned the β configuration and α configuration, respectively.

Compounds II, IIIc, IIIe, IIIh, IVa, and IVc are weak androgens, while I, IIIa, IIId, IIIf, and IIIg are inactive; none of these possesses myogenic activity at the levels tested.[10]

## Experimental Section[11]

**Reduction of 17β-Acetoxy-5α-androstan-3-one.**—A solution of 1.2 g of sodium borohydride in 100 ml of methanol and 2 ml of water was added to a solution of 10 g of 17β-acetoxy-5α-androstan-3-one in 200 ml of methanol. After 20 min at room temperature the mixture was diluted with 500 ml of water and extracted three times with ether (200, 100, 50 ml). The total ether solution was washed with 100 ml of water, dried over sodium sulfate, and evaporated, leaving 10.8 g of crude product.

**17β-Acetoxy-5α-androstan-3-yl Methanesulfonates (I and II).**—The total crude product from the sodium borohydride reduction was dissolved in 70 ml of pyridine and chilled. Methanesulfonyl chloride (16 ml) was added and the solution was refrigerated 2.5 hr. After addition of ice and cold water, the mixture was extracted with benzene. The benzene solution was washed with dilute hydrochloric acid and 5% sodium bicarbonate, dried over sodium sulfate, and evaporated. The residue was dissolved in a hot mixture of 50 ml each of benzene and petroleum ether. Cooling gave 7.04 g of compound I, mp 156.2–158.4°. Recrystallization from the same solvent gave the analytical sample: mp 158–159°; $\lambda_{max}$ 5.80 (C=O), 8.55 μ ($SO_3$).

*Anal.* Calcd for $C_{22}H_{36}O_5S$: C, 64.10; H, 8.80; S, 7.78. Found: C, 64.45; H, 8.85; S, 7.57.

The mother liquor from the first fraction was concentrated to one-half its original volume, petroleum ether (25 ml) was added, and the solution was cooled, giving 1.06 g, mp 144.6–146.2°. Dilution of the filtrate with 35 ml of petroleum ether gave another 1.55 g, mp 146.2–148°; further concentration and dilution with petroleum ether gave a final crop, 0.78 g, mp 147–149°. These fractions were identified as being predominately II with the analytical sample melting at 144–145.2° after two recrystallizations: $\lambda_{max}$ 5.78 (C=O), 8.55 μ ($SO_3$).

*Anal.* Calcd for $C_{22}H_{36}O_5S$: C, 64.10; H, 8.80; S, 7.78. Found: C, 64.34; H, 8.60; S, 7.70.

**17β-Acetoxy-5α-androstan-3α-yl Azide (IIIa).**—A solution of 7.03 g of I and 3.6 g of sodium azide in 125 ml of dimethyl sulfoxide was heated at 80–90° for 4 hr. The cooled mixture was diluted with 250 ml of water and extracted twice with ether, and the ether solution was washed twice with water. The solution was filtered, the solvent was evaporated, and the residue was dissolved in hot ethanol and then cooled to give IIIa: crop A, 4.40 g, mp 135.6–138°; crop B, 0.56 g, mp 134.8–136.5°, $\lambda_{max}$ 4.78 ($N_3$) and 5.77 μ (C=O).

*Anal.* Calcd for $C_{21}H_{33}N_3O_2$: C, 70.10; H, 9.25; N, 11.68. Found: C, 70.55; H, 9.60; N, 11.64.

**17β-Acetoxy-5α-androstan-3α-ylamine (IIIb).**—A solution of 2.60 g of IIIa and 7.8 ml of hydrazine hydrate in 100 ml of ethanol containing a teaspoon of freshly prepared Raney nickel was refluxed 5 min.[6] The mixture was cooled to room temperature, filtered, diluted with water, and extracted with ether. The ether solution was washed with water and evaporated, and the residue was dried by azeotropic distillation of benzene. The crude amine, IIIb, lacked the 4.78-μ azide band and exhibited a sharp NH band at 2.91 μ with a shoulder at 3.00 μ: it weighed 2.35 g, mp 137–141°. Recrystallization of a small portion gave an analytical sample of IIIb, mp 140–142.4°.

*Anal.* Calcd for $C_{21}H_{35}NO_2$: C, 75.50; H, 10.58; N, 4.19. Found: C, 75.20; H, 10.27; N, 4.07.

**17β-Acetoxy-5α-androstan-3α-yl Isocyanate (IIIc).**—17β-Acetoxy-5α-androstan-3α-ylamine (4.24 g) was dissolved in 50 ml of benzene and 1 ml of triethylamine and added dropwise to an ice-cooled solution of benzene kept saturated with phosgene. After 30 min, the addition was complete. The mixture was stirred and phosgene bubbled in for an additional 1.5 hr. After

(5) J. N. Tilley and H. A. R. Sayigh, *J. Org. Chem.*, **28**, 2076 (1963).

(6) C. G. Skinner, *et al.* [*Texas Rept. Biol. Med.*, **19**, 860 (1961)], synthesized a thiocarbamate with antitumor activity by condensing cysteine and methyl isocyanate.

(7) W. J. van der Burg, U. S. Patent 3,047,593 (1962).

(8) M. M. Janot, *et al.*, *Bull. Soc. Chim. France*, 1640 (1960).

(9) J. H. Boyer and F. C. Canter, *Chem. Rev.*, **54**, 1 (1954).

(10) L. G. Hershberger, E. G. Shipley, and R. K. Meyer, *Proc. Soc. Exptl. Biol. Med.*, **83**, 175 (1953).

(11) Melting points were taken on an electrically heated hot stage and are uncorrected. Infrared spectra were obtained on an Infracord on samples mulled in mineral oil. Analyses were by Galbraith Laboratories, Knoxville, Tenn., and by Midwest Microlab, Indianapolis, Ind.

a total of 3 hr the mixture was filtered and the filtrate was concentrated to dryness. The residue was taken up in ether and this solution was filtered and concentrated to give 2.29 g of crude isocyanate IIIc. The crude isocyanate was dissolved in heptane, filtered, and cooled to give crop A, 1.85 g, mp 144.4–145.8°, and crop B, 0.15 g, mp 135–139.5°. The analytical sample crystallized out of acetone–water: mp 132.8–133.8°; $\lambda_{max}$ 4.40 (NCO), 5.78 $\mu$ (C=O).

*Anal.* Calcd for $C_{22}H_{33}NO_3$: C, 73.60; H, 9.27; N, 3.90. Found: C, 73.42; H, 9.60; N, 3.84.

The N-carbethoxy derivative was prepared with ethanol: mp 165–167° (lit.[7] mp 167–169°); $\lambda_{max}$ 3.91 (NH), 5.82 (C=O), 6.18 (NH), 6.56 $\mu$ (amide II).

The benzene-insoluble material from above was combined and washed with water to remove any triethylamine hydrochloride that might be present. The solid residue was dissolved in aqueous methanolic sodium bicarbonate and reprecipitated by addition of water. The free amine (1.69 g, mp 142.4–144.4°) was recovered by extraction with ether.

**N-(17β-Acetoxy-5α-androstan-3α-yl) S-Ethylthiocarbamate (IIId).**—A solution of 150 mg of IIIc and 0.1 ml of triethylamine in 5 ml of ethanethiol stood at room temperature overnight. The solvent was evaporated at room temperature; an acetone solution of the residue was filtered and refrigerated to give the product, 144 mg, mp 169–174°. Two recrystallizations in acetone gave the analytical sample: mp 173.6–174.8°; $\lambda_{max}$ 2.96 (NH), 5.81 (C=O acetate), 6.01 $\mu$ (C=O thiocarbamate).

*Anal.* Calcd for $C_{24}H_{39}NO_3S$: C, 68.50; H, 9.32; S, 7.60. Found: C, 68.42; H, 9.62; S, 7.31.

**N-(17β-Acetoxy-5α-androstan-3α-yl)-N′,N′-di-*n*-butylurea (IIIe).**—A solution of 260 mg of IIIc in 2 ml of di-*n*-butylamine stood at room temperature overnight. The excess amine was evaporated at room temperature, and the liquid residue was chromatographed in benzene on 18 g of alumina. Fractions eluted by benzene and benzene–ether (1:1) were combined and recrysallized in heptane to give 143 mg, mp 47–55°. Two more recrystallizations in heptane raised the melting point to 50–54°. Recrystallization from acetone–water gave the analytical sample: mp 45–46°; $\lambda_{max}$ 2.95 (NH), 5.75 (C=O acetate), 6.21 $\mu$ (C=O urea).

*Anal.* Calcd for $C_{30}H_{52}N_2O_3$: C, 73.60; H, 10.72; N, 5.73. Found: C, 73.69; H, 10.69; N, 6.02.

**S-[N-(17β-Acetoxy-5α-androstan-3α-yl)carbamoyl]-L-cysteine (IIIf).**—L-Cysteine hydrochloride (555 mg) was added to a solution of 855 mg of IIIc and 20 mg of *p*-toluenesulfonic acid in 20 ml of dimethylformamide. After 4 hr at room temperature, the mixture was filtered free of a trace of sediment, chilled in an ice bath, and diluted with water. The precipitate that formed was filtered, washed with cold water until neutral washings were obtained, and finally washed with cold, aqueous acetone. The crude product [mp 173–176°, $\lambda_{max}$ 3 (br, NH), 5.77 (C=O acetate), 6 (sh, C=O thiocarbamate), 6.1–6.2 $\mu$ ($CO_2^-$)] was best purified *via* the hydrochloride.

The hydrochloride was prepared by suspending IIIf in chloroform, cooling in an ice bath, and passing in HCl gas for 30 min, during which time the solid dissolved. On further standing a new precipitate formed, 642 mg, mp 170° and 180–185°; the filtrate gave a second crop of 230 mg. A portion of the first crop was reprecipitated from chloroform–petroleum ether to give an analytical sample: mp 178–180°; $\lambda_{max}$ 3 (br, NH), 5.77 (C=O acetate and $CO_2H$), 5.98 (C=O thiocarbamate), 6.12 ($-NH_3^+$), 6.54 $\mu$ (amide II).

*Anal.* Calcd for $C_{25}H_{42}ClN_2O_5S$: C, 58.06; H, 7.99; N, 5.42; S, 6.19. Found: C, 58.42; H, 8.14; N, 5.12; S, 6.16.

**Ethyl S-[N-(17β-Acetoxy-5α-androstan-3α-yl)carbamoyl] mercaptoacetate (IIIg).**—A solution of 100 mg of IIIc in 1 ml of ethyl mercaptoacetate and 4 drops of triethylamine stood at room temperature for 3 hr. The mixture was filtered and the excess solvent was allowed to evaporate at room temperature. The crude thiocarbamate IIIg (147 mg) was dissolved in an acetone–heptane mixture, filtered, and cooled to obtain crop A, 61 mg, mp 155.8–160.2°, and crop B, 60 mg, mp 151–155°. The analytical sample was obtained by crystallizing crop A twice: mp 161.4–163.8°; $\lambda_{max}$ 2.95 (NH), 5.80, 5.97 $\mu$ (C=O).

*Anal.* Calcd for $C_{26}H_{41}NO_5S$: C, 65.10; H, 8.61; N, 2.92. Found: C, 64.76; H, 8.43; N, 2.99.

**N-(17β-Acetoxy-5α-androstan-3α-yl)-N′-carbethoxymethylurea (IIIh).**—Ethyl glycinate hydrochloride (60 mg) was suspended in 3 ml of dimethylformamide, and IIIc (100 mg) was added. After standing overnight at room temperature, the solvent was allowed to evaporate. The product was taken up in acetone–heptane, filtered, and cooled to give IIIh, 98 mg, mp 169–172°. The analytical sample crystallized out of acetone–water: $\lambda_{max}$ 2.98 (NH), 5.75, 6.17 $\mu$ (C=O).

*Anal.* Calcd for $C_{26}H_{42}N_2O_5$: C, 67.50; H, 9.15; N, 6.05. Found: C, 67.65; H, 9.09; N, 6.06.

**17β-Acetoxy-5α-androstan-3β-yl Azide (IVa).**—The reaction was carried out with 2.80 g of II and 1.40 g of sodium azide in a manner similar to the preparation of IIIa. The crude product crystallized from methanol, giving 1.20 g of IVa: mp 76.8–78.4°; $\lambda_{max}$ 4.78 ($N_3$), 5.74 $\mu$ (C=O).

*Anal.* Calcd for $C_{21}H_{33}N_3O_2$: C, 70.10; H, 9.25; N, 11.68. Found: C, 70.33; H, 9.38; N, 11.39.

Reduction of IVa with hydrazine and Raney nickel as in the reduction of IIIa gave the amine IVb, mp 106.4–107.4° from methanol, 141–145° from acetone–water.

*Anal.* Calcd for $C_{21}H_{35}NO_2$: C, 75.50; H, 10.58; N, 4.19. Found: C, 75.78; H, 10.49; N, 3.99.

The amine was converted to the amide IVd, and after two recrystallizations from MeOH gave an analytical sample: mp 286–287°, lit.[8] mp 278° (the 3α epimer has mp 185°); $\lambda_{max}$ 3.00 (NH), 5.75 (acetate C=O), 6.12 $\mu$ (amide C=O).

*Anal.* Calcd for $C_{23}H_{37}NO_3$: C, 73.56; H, 9.93; N, 3.73. Found: C, 73.55; H, 9.80; N, 3.72.

**17β-Acetoxy-5α-androstan-3β-yl Isocyanate (IVc).**—A solution of 430 mg of IVb in 25 ml of benzene and 0.2 ml of triethylamine was added dropwise to a stirred, ice-cooled solution of 30 ml of benzene kept saturated with phosgene. The mixture was cooled for 45 min; after 2.5 hr at room temperature it was refluxed 15 min and finally was concentrated to remove solvents. The residue was taken up in ether and filtered to remove triethylamine hydrochloride. Upon evaporation of the ether, 448 mg of crude isocyanate IVc was obtained. Recrystallization from heptane gave crop A, 78 mg, mp 105–110°; crop B, 200 mg, mp 95–107.2°; and crop C, 36 mg, mp 95–106°. Two recrystallizations of crop B gave the analytical sample: mp 115.8–116.5°; $\lambda_{max}$ 4.00 (NCO), 5.78 $\mu$ (C=O).

*Anal.* Calcd for $C_{22}H_{33}NO_3$: C, 73.60; H, 9.27; N, 3.90. Found: C, 73.34; H, 9.25; N, 4.05.

**Ethyl S-[N-(17β-Acetoxy-5α-androstan-3β-yl)carbamoyl]mercaptoacetate (IVe).**—Three drops of triethylamine were added to a solution of 100 mg of IVc in 1 ml of ethyl mercaptoacetate. After standing overnight at room temperature, the solution was filtered and evaporated in an open dish. The product IVe crystallized from ethyl acetate–petroleum ether to give crop A, 43 mg, mp 126–142°, and crop B, 13 mg, mp 134.8–145°. Recrystallization of combined crops A and B gave the analytical sample: 35 mg; mp 149–151°; $\lambda_{max}$ 2.95 (NH), 5.80, 5.97 $\mu$ (C=O).

*Anal.* Calcd for $C_{26}H_{41}NO_5S$: C, 65.10; H, 8.61; S, 6.68. Found: C, 65.09; H, 8.87; S, 6.87.

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