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C-10 SUBSTITUTED 19-NORSTEROIDS—VII

10-CYANO-2-KETOSTEROIDS[1a,b]

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Abstract—The syntheses of 10α- and 10β-cyano-5α-estran-2-one-17β-ol is described. Some reactions of the new compounds are described and discussed.

THE addition of the elements of hydrogen cyanide to a $\Delta^{1(10)}$-2-ketosteroid is a most valuable procedure for the introduction of C-10 angular function into the molecule.[4] The compound 1, synthesized in these laboratories,[5] has been employed for the preparation of the cyanosteroids IIa and IIIa. This sequence has the advantages over the previously described Grignard addition,[1] in that the cyano group can be readily transformed into a variety of other functions.

The reaction of 17β-hydroxy-5α-estra-1 (10)-en-2-one (I)[5] with potassium cyanide in the presence of ammonium chloride proceeded smoothly to yield two isomeric cyanoketones which were sparated by fractional crystallization. The 10α-cyano-2-ketone IIa m.p. 187° was isolated in 50% yield, and 20% of the 10β-cyano compound IIIa m.p. 215° was obtained. The structures of the two isomers were initially assigned from their ORD spectra,[6] that of IIa corresponding to a 5β-3-ketone, with a negative Cotton effect and that of IIIa to a 5α-3-ketone, with a positive one.[7] The higher yield of the *cis*-10α-isomer (Ia) in the cyanation reaction is noteworthy, since in the hydrocyanation of the similar angular C-13 position in D-homo derivatives the *trans* product usually predominated.[8] The larger proportion of the α product cannot be ascribed only to steric preference as with the Grignard addition product,[9] since the cyanation reaction appears not to be subject to steric control.[10,11] Use of cyanating conditions which normally lead to *trans* product predominance,[12] in this case increased the yield of the *trans*-10β-cyanoketone (IIIa) only slightly. The NMR spectra of the new cyanoketones were particularly interesting because the cyano group in each case exhibited a long range deshielding effect on the C-18 methyl protons. Thus, the 10α-cyano group shifted the C-18 methyl proton absorption downfield by 2 c/s compared to the 10α-methyl compound,[1] while the 10β-cyano group induced a 4 c/s downfield

[1a] Part VI, J. A. Settepani, M. Torigoe and J. Fishman, *Tetrahedron* **21**, 3661 (1965).
[1b] Part of this work has been presented at the VI*th Pan-American Congress of Biochemistry and Pharmacology* Mexico City, December 10 (1963).
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[3] To whom any inquiries regarding this paper should be addressed.
[4] M. Torigoe and J. Fishman, *Tetrahedron Letters* No. 19, 1251 (1963).
[5] J. Fishman and M. Tomasz, *J. Org. Chem.* **27**, 365 (1962).
[6] These spectra were obtained through the courtesy of Professor Carl Djerassi, Stanford University.
[7] C. Djerassi and W. Closson, *J. Amer. Chem. Soc.* **80**, 1216 (1958).
[8] W. Nagata, *Tetrahedron* **13**, 278 (1961).
[9] H. Mori, *Chem. Pharm. Bull., Tokyo* **12**, 1224 (1964).
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shift compared to the corresponding 10β-methyl compound.[13] This result is in agreement with the 5-cyano derivatives[14] where a deshielding of the C-19 methyl protons was observed rather than the expected shielding. The explanation of this effect in the C-5 substituted compounds was the magnetic anisotropy of the C—C≡N single bond, and the effect of C—C≡N dipole on the magnetic environment of the C-19 methyl group.[14] Similar considerations apply to the 10-cyanosteroids except that the effects on the C-18 methyl protons are smaller because of the longer distance.

Various reactions of the isomeric cyanoketones IIa and IIIa were studied in order to disclose any differences due to steric orientation. These reactions led to new products of interest, particularly in the 10α series, and it was further possible to correlate the cyanoketones IIa and IIIa with known compounds and thus confirm the structures initially assigned to them. With ethylene glycol the 10α-cyanoketone IIa gave an oily dioxolane derivative IVa which was converted to a crystalline 17-acetate IVb with a double m.p. 192–194°/205–207°. The yield of IVa was about 60%, in contrast to the better than 90% yield of the 10β-cyanoketal Va obtained under identical conditions. LAH reduction of IVa for 2 hr at room temperature, after hydrolysis with base followed by acetylation gave a 40% yield of 2,2-ethylenedioxy-10α-formyl-5α-estran-17β-ol acetate (VI) m.p. 194–197°. In addition, an approximately equal amount of the 10α-aminomethyl diacetate (VII) was obtained as the product of reduction beyond the imine stage. Reduction of the 10β-cyanoketal Va with LAH in tetrahydrofuran required prolonged reflux, and the product, after hydrolysis and acetylation was the 10β-aldehyde (IX) obtained in 60% yield. A small amount of diol monoacetate was also obtained to which we assign tentatively the 2,2-ethylenedioxy-5α-estran-10ξ,17β-diol-17 acetate structure (X).* The amino compound [VIII] comparable to that obtained from the 10α series appeared to be absent. This difference in the ease of reduction of the isomeric C-10 cyano groups clearly indicates the much greater availability to attack of the 10α-cyano moiety. Not only is the 10α cyano group equatorial with respect to ring B, while the 10β substituent is axial to both rings A and B, but the steric influence of the 18β-methyl group is missing. Therefore, it is not surprising that the difference in reactivity between the 10α and 10β-cyano groups is at least of the same magnitude as that between the 5β- and 5α-cyano series where only the conformational factors apply.[11,15]

Subsequent reduction with LAH of the 10α-aldehyde (VI) gave 2,2-ethylenedioxy-5α,10α-androstan-17β,19-diol (XI) m.p. 192–194° in quantitative yield. Wolf-Kishner reduction of the aldehyde (VI) gave the 10α-methyl compound (XII) which on deketalization, afforded 2-oxo-5α,10α-androstan-17β-ol (XIII) identical with that obtained by other routes.[1,16] This confirmed both the original 10α-cyano-2-keto structure (IIa), and, by inference, the isomeric 10β-cyano structure (IIIa) as well.

In an attempt to elaborate further the 2-keto-10-cyano steroid, with the aim of introducing oxygen at carbon 3, IIa was converted to the thioketal (XIV) but only in

* An analogous formation of a 13-hydroxy steroid during the reduction of a 13-cyano compound has been reported; M. M. Janot, X. Lusinchi and R. Goutarel, *C.R. Acad. Sci., Paris* **258**: 4780 (1964). We are grateful to the referee for bringing this report to our attention.

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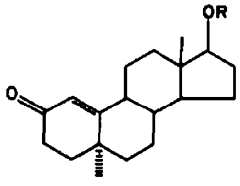
60% yield. The corresponding 10β-cyanothioketal (XV) was obtained from IIIa in quantitative yield, a further illustration of greater access to the ketone in the *trans*-10β-cyano structure. A similar observation was also made in the 5-cyano-3-keto series[11] where the *trans*-ketone also reacted more readily. Reflux of the thioketal (XIV) with Raney nickel in acetone[17] gave an olefin (XVI) in a 60% yield with the double bond either at C-1 or C-2. On the basis of the enolization direction of the 5α,10α-2-ketone,[1] a preference for the C-2 double bond could be expected; however in view of the subtle factors responsible for the relative stabilities of each of the possible positions[18] in ring A, no decision can be made on this basis. The double bond in XVIb was readily reduced with hydrogen to yield the saturated 10α-cyano-5α-estran-17β-ol acetate (XVII). For comparison, the Raney nickel desulfurization in acetone was repeated with 10β-cyano-2-thioketal, XV and gave on olefin in 50% yield. The location of the double bond in the new olefin (XVIII) is also undetermined, but the Δ^2-position is suggested by the vinyl proton resonance in the NMR spectrum, which is almost superimposable with the vinyl protons in 5α-cyano-estra-2-en-17β-ol acetate.[11] It was obvious that the Δ^2-compounds would be suitable for the introduction of oxygen at the C-3 position. However, since alternative and superior methods for the preparations of 10-cyanosteroids with an oxygen at C-3 became available,[19] the question of the location of the double bond in olefins XVI and XVIII was of less immediate interest and was not further pursued.



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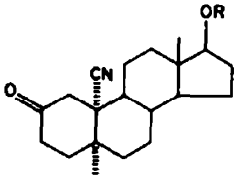

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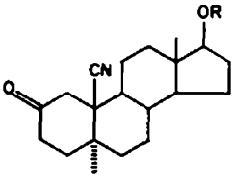

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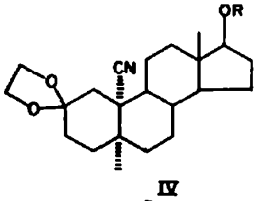

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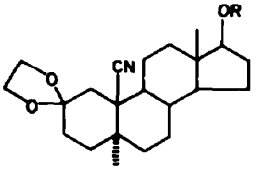

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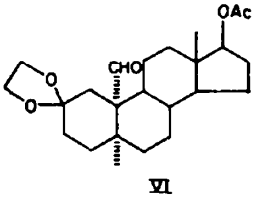

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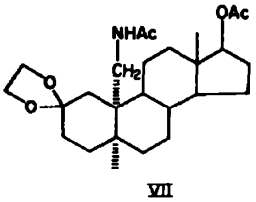

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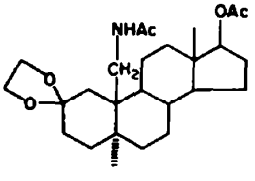

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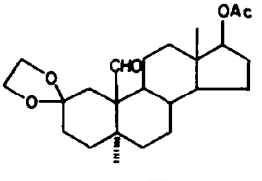

IX

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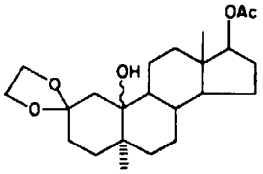
[18] L. F. Fieser and M. Fieser, *Steroids* p. 276. Reinhold, New York (1959).
[19] J. Fishman, M. Torigoe and J. A. Settepani, *Tetrahedron* **21**, 3677 (1965).



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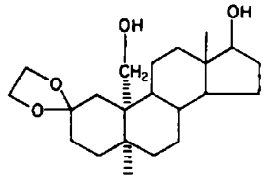

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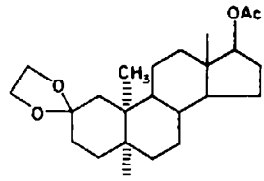

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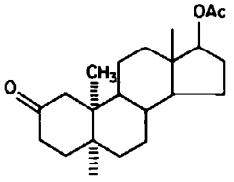

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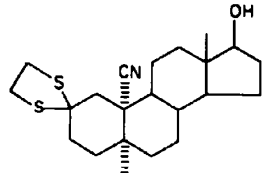
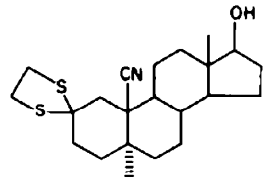


XIV



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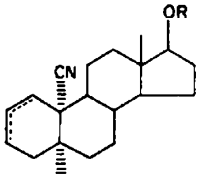

XVI
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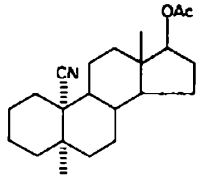
b R=CH3CO



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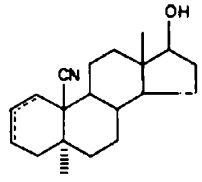

XVIII

EXPERIMENTAL[30]

Hydrocyanation of 17β-*hydroxy*-5α-*estra*-1 (10)-*en*-2-*one* (I)

(a) A mixture of 1·0 g I, 480 mg KCN and 340 mg NH_4Cl in 17 ml MeOH and 4 ml water was refluxed under N_2. After 1¾ hr the UV absorption at 237 mμ was 10% of the original and did not show any further decrease. At the end of 2 hr the MeOH was removed *in vacuo*, 100 ml water was added and the aqueous mixture extracted with ethyl acetate. The organic layer was dried and evaporated and the residue was crystallized from MeOH to give 389 mg IIa m.p. 180–184°. An additional crop of 146 mg m.p. 178–182° was obtained from the mother liquors. The total yield of IIa was 49%. The remaining mother liquor was taken to dryness and the residue recrystallized from ethyl acetate to give 235 mg IIIa m.p. 211–213°, representing about 21% yield.

The analytical sample of 10α-*cyano*-17β-*hydroxy*-5α-*estran*-2-*one* (IIa) was obtained from MeOH and melted 185–187°C. $[\alpha]_D^{24}$ +38. ORD $\alpha_{540} = 0°$, $\alpha_{350} = 50°$, $\alpha_{318} = 0°$, $\alpha_{300} = -167°$, $\alpha_{260} = 655°$. (Found: C, 75·81; H, 9·04; N, 4·59. Calc. for $C_{19}H_{27}O_2N$: C, 75·71; H, 9·03; N, 4·65%.)

The *acetate* IIb which was prepared in the usual manner was recrystallized from MeOH and melted 203–204° $[\alpha]_D^{25}$ +25°.

NMR ($CDCl_3$) singlets (3H) at 48 c/s ($18CH_3$) 122 c/s (17 Ac). (Found: C, 72·98; H, 8·80. Calc. for $C_{21}H_{29}O_3N$: C, 73·43; H, 8·51%.)

The analytical sample of 10β-*cyano*-17β-*hydroxy*-5α-*estran*-2-*one* (IIIa) was obtained from ethyl acetate and melted at 215–216°. $[\alpha]_D^{24}$ +40°. ORD $\alpha_{480} = 0°$, $\alpha_{305} = 735°$, $\alpha_{258} = -1070°$, $\alpha_{240} = -900°$. (Found: C, 75·60; H, 8·89; N, 4·96. Calc. for $C_{19}H_{27}O_2N$: C, 75·71; H, 9·03; N, 4·65%.)

[30] The m.ps were obtained on a Koffler block and are corrected. NMR spectra were determined on a Varian A60 instrument. Values given are in c/s downfield from tetramethylsilane at 0 c/s as an internal standard. Rotations were in $CHCl_3$ solution unless otherwise stated. The IR spectra were determined in KBr. Analyses are by Spang Analytical Laboratories.

The *acetate* IIIb, was also prepared in the usual manner with acetic anhydride in pyridine. After two crystallizations from pet. ether–acetone it melted 176–178°.

NMR ($CDCl_3$) singlets (3H) at 52 c/s (18 CH_3); 122 c/s (17 Ac). (Found: C, 73·24; H, 8·46. Calc. for $C_{21}H_{33}O_3N$: C, 73·43; H, 8·51%.)

(b) To an ice cooled solution of 105 mg Ib in 10 ml tetrahydrofuran was added a solution of Et_2Al and HCN[21] in 10 ml tetrahydrofuran, containing 25 mg HCN and 100 mg Et_2Al. The mixture was allowed to stand at room temp for 1 hr and was then added slowly to 10 ml of an ice cold 2N NaOH solution. The alkaline solution was then extracted with $CHCl_3$ which was dried and evaporated. The residue crystallized from MeOH to give 46 mg IIa m.p. 178–182°. The residue from the mother liquors yielded 28 mg IIIa m.p. 210–13° on crystallization from ethyl acetate.

2,2-Ethylenedioxy-10α-cyano-5α-estran-17β-ol acetate (IVb)

To a solution of 500 mg IIa in 200 ml dry benzene was added 1·5 ml ethylene glycol and 50 mg *p*-toluenesulfonic acid. The solution was refluxed slowly in a flask equipped with a Dean-Stark separator. After 7 hr the benzene solution was washed with Na_2CO_3aq and water, dried and evaporated. The residue was an oil which could not be induced to crystallize, and which contained 30% of the original carbonyl absorption in the IR. Chromatography on alumina and elution with pet. ether–benzene gave IVa as an oil which lacked any carbonyl absorption in the IR. After overnight acetylation with acetic anhydride in pyridine followed by the usual workup the product could be crystallized from acetone–pet. ether to give 376 mg IVb with a m.p. 192–195°, (203–205°). $[\alpha]_D^{24}$ +20°. (Found: C, 71·26; H, 8·84. Calc. for $C_{23}H_{33}O_4N$: C, 71·29; H, 8·58%.)

2,2-Ethylenedioxy-10β-cyano-5α-estran-17β-ol (Va)

A 100 mg sample of IIIa was reacted with ethylene glycol in the presence of *p*-toluenesulfonic acid as described above. The product crystallized from acetone–pet. ether to give 108 mg Va m.p. 200–202°. The analytical sample also obtained from the same solvents melted 201–203°. (Found: C, 72·74; H, 9·26; N, 4·32. Calc. for $C_{21}H_{31}O_2N$: C, 73·00; H, 9·05; N, 4·05%.)

The *acetate* Vb prepared in the usual manner crystallized from MeOH m.p. 226–227°. (Found: C, 71·13; H, 8·84; N, 3·81. Calc. for $C_{23}H_{33}O_4N$: C, 71·29; H, 8·58; N, 3·61%.)

LAH *Reduction of* IVa

A suspension of 50 mg LAH in 20 ml tetrahydrofuran was added to a stirred, ice cooled solution of 250 mg IVa in 50 ml tetrahydrofuran. After stirring at room temp for 1 hr, 20 ml ice cold water was added cautiously followed by 5 ml 2N NaOH solution and the mixture was refluxed in a N_2 atm. for 10 mins. The product was extracted with $CHCl_3$ which was washed with water, dried and evaporated and the residue was acetylated overnight with acetic anhydride in pyridine. The usual workup gave a semicrystalline material which was recrystallized from MeOH to give 92 mg of *2,2-ethylenedioxy-10α-aminomethyl-5α-estran-17 β-ol diacetate* (VII) m.p. 138–142°

The mother liquor was taken to dryness and the residue chromatographed on 14 g acid washed alumina. Elution with benzene gave 145 mg material which on crystallization from acetone afforded 104 mg *2,2-ethylenedioxy-10α-formyl-5α-estran-17β-ol acetate* (VI) as prisms m.p. 192–195° with dec.

The analytical sample of the *amine* VII melted with dec at 140–142°. NMR ($CDCl_3$) 46 c/s (18 CH_3), 122 c/s (both acetates), 372 c/s (Amide H). (Found: C, 69·41; H, 8·89; N, 3·42. Calc. for $C_{25}H_{39}O_5N$: C, 69·25; H, 9·07; N, 3·23%.)

The analytical sample of the *aldehyde* VI melted 195–197°. $[\alpha]_D^{25}$ +3°. Aldehyde CH stretching absorption in the IR was at 2730 cm^{-1}. (Found: C, 7085; H, 9·10. Calc. for $C_{23}H_{34}O_5$: C, 70·74; H, 8·78%.)

LAH *Reduction of* Va

A solution of 40 mg LAH in 5 ml tetrahydrofuran was added to a solution of 50 mg Va in 10 ml tetrahydrofuran. The mixture was refluxed for 17 hr, after which 4 ml water were added slowly followed by 1 ml 2N NaOH solution. The mixture was then refluxed for 10 min under a N_2 atm and was extracted with $CHCl_3$ which was dried and evaporated. The residue was acetylated and after

[21] The authors wish to thank Dr. Wataru Nagata, for kindly providing the experimental details for this reaction.

workup gave 54 mg of oil which was chromatographed on acid washed alumina. Elution with pet. ether–benzene 1:1 gave 7 mg of crystals m.p. 195–199°. For analysis it was recrystallized from acetone to give 2,2-*ethylenedioxy*-5α-*estran*-10ξ,17β-*diol*-17 *acetate* (X) m.p. 197–199°. The compound showed hydroxyl absorption in the IR at 3530 cm^{-1}. (Found: C, 70·04; H, 9·21. Calc. for $C_{22}H_{34}O_5$: C, 69·81; H, 9·05%.)

Further elution with benzene gave 32 mg 2,2-*ethylenedioxy*-10β-*formyl*-5α-*estran*-17β-*ol acetate* (IX) m.p. 181–186°, with dec. For analysis the sample was recrystallized from MeOH and melted at 187–190° dec. The CH stretching aldehyde absorption in the IR was at 2742 cm^{-1}. (Found: C, 70·96; H, 9·02. Calc. for $C_{23}H_{34}O_6$: C, 70·74; H, 8·70%.)

2,2-*Ethylenedioxy*-5α,10α-*androstane*-17β,19-*diol* (XI)

A solution of 36 mg of VI in 5 ml ether was added to a stirred suspension of 20 mg LAH in 10 ml ether. After refluxing for 1 hr water was added dropwise and the mixture was extracted with ether, which was dried and evaporated. The product was crystallized from $CHCl_3$ as short prisms m.p. 192–194°, containing some solvent which was lost on heating at 100°. The yield of XI was 35 mg and the product showed no carbonyl absorption in the IR. (Found: C, 71·99; H, 9·87. Calc. for $C_{21}H_{34}O_4$: C, 71·96; H, 9·78%.)

2,2-*Ethylenedioxy*-5α,10α-*androstan*-17β-*ol acetate* (XII)

A solution of 30 mg of VI, 106 mg KOH and 0·3 ml hydrazine hydrate in 2 ml triethylene glycol was heated at 135° for 1 hr. The condenser was then removed and the temp was raised to 210–220°. After 1·5 hr at this temp the solution was poured into ice water and extracted with $CHCl_3$ which was washed with water, dried and evaporated. The residue was acetylated overnight and after workup gave 34 mg crystalline material which was recrystallized from MeOH to give 25 mg XII m.p. 166–167°, having no aldehyde absorption in the IR. (Found: C, 72·89; H, 9·81. Calc. for $C_{23}H_{36}O_4$: C, 73·36; H, 9·64%.)

17β-*Acetoxy*-5α,10α-*androstan*-2-*one* (XIII)

A solution of 10 mg XII in 10 ml acetone and 2 ml 2N HCl solution was refluxed for 2 hr. Water was then added, and the mixture was extracted with $CHCl_3$ which was washed with water, dried and evaporated. The residue isolated after overnight acetylation was recrystallized from acetone to give 8·7 mg XIII m.p. 197–199°, identical in all respects with that prepared by other routes.[1,16]

2,2-*Ethylenedithio*-10α-*cyano*-5α-*estran*-17β-*ol* (XIV)

A mixture of 605 mg IIa, 12 g freshly fused $ZnCl_2$, 12 g Na_2SO_4, 2·4 ml ethanedithiol in 36 ml dioxan was allowed to stand overnight at room temp. It was then poured into excess dil. NH_4OHaq, and the precipitate was filtered off. The precipitate was dissolved in acetone, filtered and the filtrate was taken to dryness. The residue was crystallized from ethyl acetate to give 460 mg of XIV m.p. 201–203°. The mother liquor contained mainly starting material.

The analytical sample of XIV melted at 202–203° $[\alpha]_D^{23}$ +51°. (Found: C, 66·88; H, 8·08. Calc. for $C_{21}H_{31}ONS_2$: C, 66·82; H, 8·28%.)

2,2-*Ethylenedithio*-10β-*cyano*-5α-*estran*-17β-*ol* (XV)

A 231 mg sample of IIIa was reacted with ethanedithiol exactly as above. The product crystallized from ethyl acetate to give 270 mg XV m.p. 208–210°. $[\alpha]_D^{24}$ +26°. (Found: C, 66·88; H, 8·21. Calc. for $C_{21}H_{31}ONS_2$: C, 66·82; H, 8·28%.)

Raney nickel desulfurization of XIV

Approximately 9 g of W2 Raney Ni was added to a solution of 450 mg XIV in 300 ml acetone. The mixture was refluxed for 4 hr after which the Ni was filtered off and washed well with acetone. The solvent was evaporated and the crystalline residue was recrystallized twice from MeOH and once from ether to give 185 mg of XVIa m.p. 162–164°, which showed the presence of unsaturation in the IR at 3040, 1660 cm^{-1}, $[\alpha]_D^{23}$ +39°. (Found: C, 79·89; H, 9·82. Calc. for $C_{19}H_{27}ON$: C, 79·95; H, 9·54%.)

The *acetate* XVIb prepared in the usual manner was recrystallized from MeOH and melted at 150–152°. (Found: C, 77·12; H, 8·84. Calc. for $C_{21}H_{29}O_2N$: C, 77·02; H, 8·93%.)

Raney nickel desulfurization of XV

A 30 mg sample of XV was reacted with Raney Ni in acetone as described above. The product could not be crystallized and was chromatographed on alumina. Elution with pet. ether–benzene mixture 1:1 gave 19 mg of crystalline material which was recrystallized from benzene–pet. ether to yield 12 mg of needles m.p. 168–171°. The presence of unsaturation was indicated by IR absorption bands at 3020 and 1655 cm^{-1} and the downfield vinyl proton resonance as a doublet at 342 c/s in the NMR. The analytical sample of the olefin XVIII melted at 169–172°. (Found: C, 79·53; H, 9·78; N, 4·61. Calc. for $C_{19}H_{27}ON$: C, 79·95; H, 9·54; N, 4·31%.)

10α-*cyano*-5α-*estran*-17β-*ol acetate* (XVII)

A solution of 20 mg of XVIb in 2 ml EtOH was hydrogenated for 10 min over 5 mg of 10% PdC. After isolation, the product was crystallized from MeOH to give 12 mg XVII m.p. 157–158°, depressed to 140–155° on admixture with the starting material. There was no evidence of unsaturation in either the IR or NMR spectra. (Found: C, 76·48; H, 9·39. Calc. for $C_{21}H_{31}O_2N$: C, 76·55; H, 9·48%.)

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