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Studies on Conformation and Reactivity. X.[1] The Synthesis and Transannular Cyclization of 17β-Benzoyloxy-2α-hydroxy-5β-androstane leading to 17β-Benzoyloxy-2α,9α-epoxy-5β-androstane[2]

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17β-Benzoyloxy-2α-hydroxy-5β-androstane (XIb), the key intermediate for the transannular cyclization reaction from 2C to 9C in the 5β-androstane system, was synthesized from testosterone (III) in six steps and in the overall yield of 17.6% *via* the intermediacy of 2α-hydroxy-4-en-3-oxo system (VII). The stereochemistry of the epoxidation of the 4-en-3-oxo system (III) with alkaline hydrogen peroxide was established, the reaction favoring the formation of the 4β,5-epoxide (IVb) to the formation of the 4α,5-isomer (IVa) in the relative ratio of 5:1. Meanwhile, oxidation of XIb with Jones reagent afforded the 2-oxo-5β system (XIIIb) which exhibits negative Cotton effect curves with much weaker intensity compared with that of positive Cotton effect curves exhibited by the 2-oxo-5α system(XIIIa).

Treatment of XIb with lead tetraacetate in benzene afforded 17β-benzoyloxy-2α, 9α-epoxy-5β-androstane (XVII). The 17β-acetoxy analogue(XIX) of the 2α,9α-epoxide (XVII) was converted to the 9α,11α-epoxide system (XXII) *via* the 9(11)-eno intermediate (XXI). Reductive cleavage of XXII with lithium–ethylamine afforded the 2α,9α,-17β-trihydroxy-5β-androstane (XXIII) which gave 2α, 17β-diacetate (XXIV).

Sterically controlled functionalization reaction at inactive carbon atom is a useful reaction as it can lead to the introduction of a desirable hetero function selectively onto a certain carbon atom which can hardly react toward reagents under general conditions.

Inspection of stereomodels of the 5β-steroid system shows that the 2α-hydroxy-5β-steroid system (I) might have a close proximity between the 2α-O and 9α-H atoms and would favor a ring closure between these functions under suitable oxidative condition forming a new steroidal tetrahydrofuran (II). The reaction can be certainly a sterically controlled functionalization at an inactive carbon atom or 9C in the steroid nucleus, and also may lead to new and valuable steroid heterocycles with unique biological activities.

With these motives in mind, the synthesis and transannular cyclization of previously unknown 2α-hydroxy-5β system (I) have been attempted and successful in the cholestane series.[4] The reactions then appeared to be useful and of value to apply to other steroid systems with different structural features and with unique biological activities for further development and generalization of the reactions. The 17β-hydroxyandrostane series were therefore chosen for further investigation. We could succeed in the synthesis of previously unknown 17β-benzoyloxy-2α-hydroxy-5β-androstane (XIb) from 17β-hydroxyandrost-4-en-3-one (testosterone) (III) in six steps and its transannular cyclization at 9C with lead tetraacetate leading to the 2α,9α-epoxide (XVII). The stereochemistry of the reactions were completely established. The present paper describes the synthesis of the 2α-hydroxide (XIb) as the key intermediate, the cyclization reaction, the conversion of the epoxide (XVII) to the 9α,11α-epoxide (XXII) *via* the 9(11)-eno intermediate (XXI), the reductive cleavage of XXII to the 2α,9α,17β-trihydroxy-5β system (XXIII), and the stereochemistry of those

1) Part IX: J. Yoshizawa and M. Tomoeda, *J. Chem. Soc.* (*C*), **1971**, 1741.
2) Presented at the 87th Annual Meeting of the Pharmaceutical Society of Japan, Kyoto, April, 1967.
3) Location: *Takara-machi, Kanazawa.*
4) T. Koga and M. Tomoeda, *Tetrahedron*, **26**, 1043 (1970).

new steroids. The paper also contains results on the stereochemistry of the epoxidation of the 4-en-3-oxo system in the 17β-hydroxyandrostane series as a correction of data previously reported in the literature.[5,6]

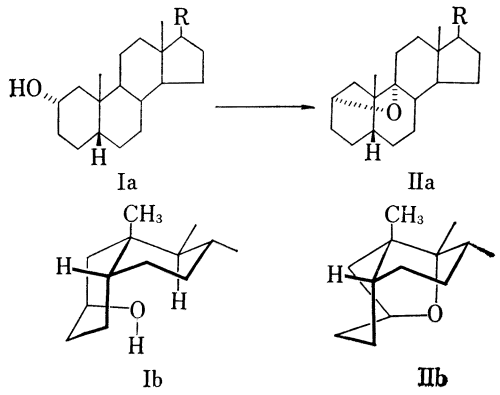


Chart 1

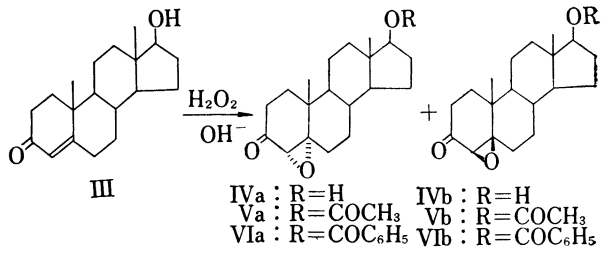


Chart 2

The 2α-hydroxide (XIb) was synthesized from testosterone (III) in six steps and in the overall yield of 17.6% as follows. Testosterone (III) was subjected to alkaline hydrogen peroxide oxidation in methanol[5] affording 4β,5-epoxy-17β-hydroxy-5β-androstan-3-one (IVb) and the 4α,5-isomer (IVa) in 65.3% and 13.5% yields respectively. The structure of the 4β,5-epoxide (IVb) of mp 159.5—160° and $[\alpha]_D^{28}$+148.9° was supported by the microanalysis, mass spectrum and other physical properties. The mp and specific rotation of the compound were in agreement with the literature.[5] The structure of the 4α,5-isomer (IVa) of mp 172—173° and $[\alpha]_D^{26}$—64.6° was verified in the similar way as with IVb. However, the mp and specific rotation were not in agreement with the literature[5] which reported mp 147—148° and $[\alpha]_D$—33°.

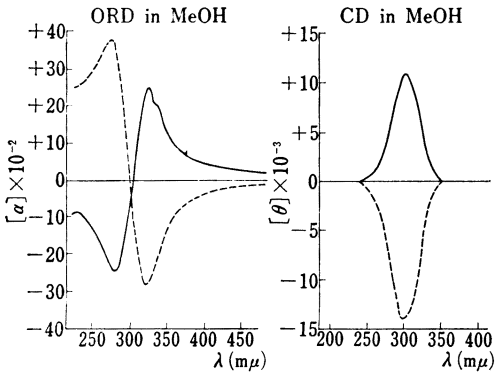
Confirmation of the structures and configurations of these isomeric IVa and IVb was carried out as follows. The assignment of α or β configurations at 4C and 5C for IVa or IVb was supported by the nuclear magnetic resonance (NMR) spectra showing the 19-methyl peak for IVb at a position (τ 8.84) which is 0.09 ppm lower than the 19-methyl peak for IVa. Furthermore, IVa and IVb show in their optical rotatory dispersion (ORD) and circular dichroism (CD) curves symmetrical Cotton effects with negative and positive signs respectively, as shown in Fig. 1. The opposite signs of Cotton effects shown by IVa and IVb can be understood by applying the "reversed" Octant Rule[7] to the isomeric epoxyketone system fused to A rings in the compounds. Acetylation of IVa and IVb with acetic anhydride in pyridine gave their corresponding 17β-acetates, Va of mp 169.5—171° and Vb of mp 160.5—161.5° in 98.9% and 98.0% yields respectively. The mp and specific rotations of these acetates were found to be in agreement with those reported in the literature.[5] The 4α,5-epoxide (IVa) and its 4β,5-isomer (IVb) were also converted to their corresponding 17β-benzoates, VIa of mp 170.5—171.5° and VIb of mp 177—178° in 98.9% and 99.8% yields respectively.

All these data confirmed the configuration at 5C of IVb to be β and that of IVa, α. Then the compound of mp 147—148° and $[\alpha]_D$—33° reported as 4α,5-epoxide by the literature[5] appeared to be a mixture of IVa and IVb. It is now summarized that alkaline hydrogen

5) B. Camerino, B. Pattelli and A. Vercellone, *J. Am. Chem. Soc.*, **78**, 3540 (1956).
6) H. B. Henbest, *Proc. Chem. Soc.*, **1963**, 159.
7) M. Legrand, R. Viennet and J. Caumartin, *Compt. Rend.*, **253**, 2378 (1961); C, Djerassi, W. Klyne, T. Norin, G. Ohloff and E. Klein, *Tetrahedron*, **21**, 163 (1965).

peroxide oxidation of testosterone (III) in methanol gives the 4α,5-epoxide (IVa) and its 4β,5-isomer (IVb) in a relative ratio of 1: 5, and that the relative formation ratio of those epoxides as 3: 7 reported by Henbest[6] should be corrected.

Now, the 17β-acetoxy-4β,5-epoxide (Vb) was chosen as the starting material for the subsequent reactions and was subjected to abnormal acid ring opening[8] with dil. H_2SO_4 in acetone. However, the reaction resulted in the hydrolysis of the 17β-acetoxy group as the major line and the formation of the 2α-hydroxy-Δ^4-3-ketone system as the very minor line; formation of the latter compound could be only detected by thin-layer chromatography (TLC). The 17β-acetoxy-Vb was then replaced by the 17β-benzoyloxy-VIb, which was subjected to the abnormal ring opening affording 17β-benzoyloxy-2α-hydroxyandrost-4-en-3-one (VII) of mp 199—201.5° in good yield (85.9%). The microanalysis and mass spectrum were in agreement with the structure. The ultraviolet (UV) and infrared (IR) spectra show absorptions due to the 4-en-3-oxo system and the benzoyloxy group. The NMR spectrum shows two singlet peaks for the 4-vinylic proton and also for the 10-methyl group under a deshielding effect of the 4-en-3-oxo system.[9] The NMR spectrum further exhibits a quartet with a large J assignable to the 2β-hydrogen of the axial character.[10]



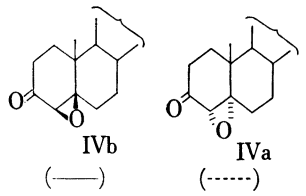


Fig. 1. ORD and CD Curves of 4α, 5-Epoxy-17β-hydroxy-5α-(IVa) (·····) and 4β, 5-Epoxy-17β-hydroxy-5β-(IVb) (——) -androstan-3-ones in Methanol Solution

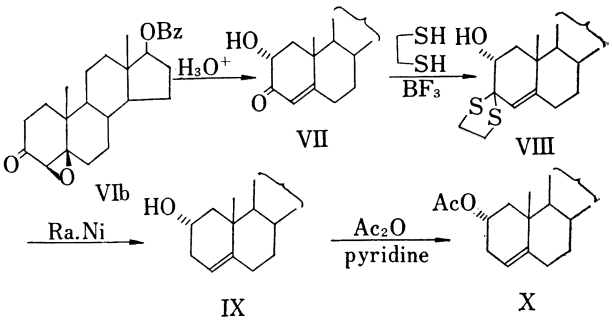


Chart 3

When VII was treated with ethanedithiol in glacial acetic acid using boron trifluoride etherate as catalyst, 17β-benzoyloxy-2α-hydroxyandrost-4-en-3-one ethylenethioketal (VIII) of mp 245.5—246.5° was obtained in 99.9% yield. The microanalysis and mass spectrum were in agreement with the structure. The NMR spectrum shows a triplet assignable to the -S-CH_2-CH_2-S- group at 3C. The other spectroscopic evidence supported the structure.

The ethylenethioketal (VIII) was then desulfurized by treatment with Raney Ni in boiling ethanol to give 17β-benzoyloxy-2α-hydroxyandrost-4-ene (IX) of mp 76—83° in 97.8% yield. The compound resisted crystallization, however, the structure was verified by the physical properties. The NMR spectrum did not display the peak due to the -S-CH_2-

8) M. Tomoeda, M. Ishizaki, H. Kobayashi, S. Kanatomo, T. Koga, M. Inuzuka and T. Furuta, *Tetrahedron*, **21**, 733 (1965).
9) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, 1964, p. 13.
10) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p. 84.

CH_2-S- group but the peak due to the 4-eno system. The fact that acetylation of IX with acetic anhydride in pyridine afforded the corresponding acetate X, gave a further support for the structure of IX.

The 2α-hydroxy-4-eno compound (IX) was subjected to catalytic hydrogenation in 99% ethanol with 20% Pt-charcoal as catalyst, affording isomeric 17β-benzoyloxy-2α-hydroxy-5β-androstane (XIb) of mp 144—145° and its 5α-isomer (XIa) of mp 175.5—176.7° in 32.2% and 16.9% yields[4] respectively. Added to XIa and XIb, a third crystalline compound of mp 72—88° was obtained. The compound does not show any characteristic absorption in its IR spectrum due to any functional group except absorptions due to the 17β-benzoyloxy group, and was suggested to be a further hydrogenated product, 17β-benzoyloxy-androstane. However, further confirmation of the structure was not carried out.

The microanalyses, mass, UV and IR spectra were consistent with the structures and configurations assigned for isomeric XIa and XIb. Any absorption due to the 4-eno group was no longer present in their UV or IR spectra but absorptions due to the 2α-hydroxyl groups and the 17β-benzoyloxy groups are present in the IR spectra. The NMR spectra did not display the presence of 4-vinylic protons. Evidence for the assignment of α configuration at 2C for XIa and XIb was provided by the fact that the NMR spectra show a peak with a smaller half width at a lower field for the 2β-proton of XIb than for the same hydrogen of XIa. It led to the conclusion that the 2β-hydrogen of XIb is equatorial and that of XIa, axial,[4,10] and that the configuration at 5C of XIb should then be β and that of XIa, α. The assignment of these configurations for XIa and XIb was supported by the fact that XIb with the axial hydroxyl group is eluted faster from a chromatogram than XIa with the equatorial hydroxyl group. The structures and configurations of XIa and XIb were further supported by the fact that acetylation (acetic anhydride and pyridine) of XIb takes about ten times longer than the case of XIa, affording the corresponding acetates, XIIa of mp 202—203.5° and XIIb of mp 158.5—159.5° respectively. Meanwhile, the 2α-

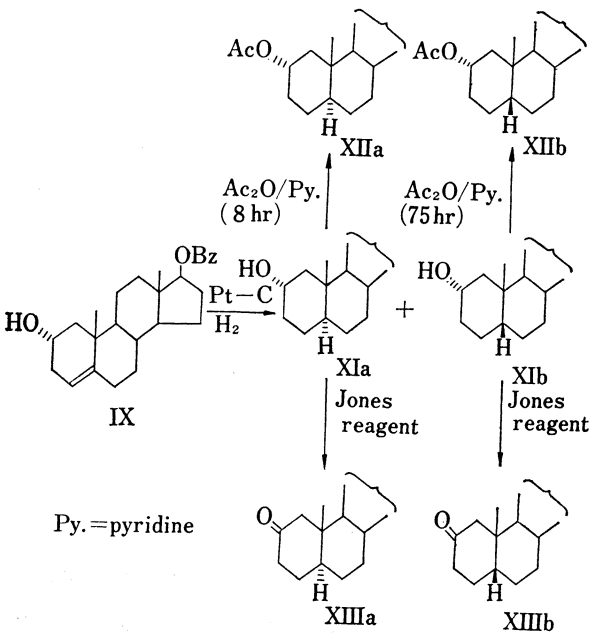


Chart 4

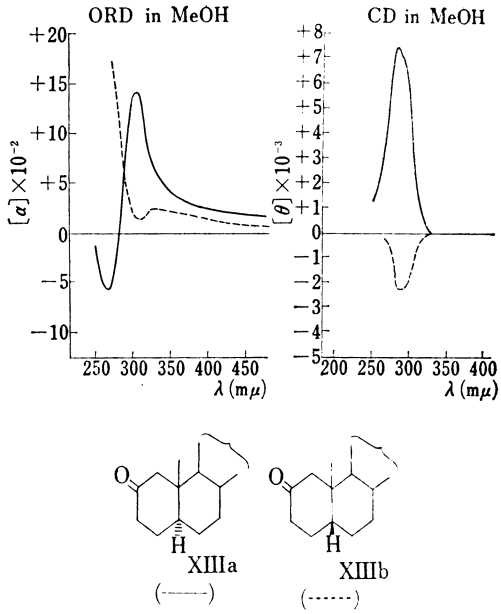


Fig. 2. ORD and CD Curves of 17β-Benzoyloxy-2-oxo-5α-(XIIIa) (——) and -5β-(XIIIb) (------) Androstanes in Methanol Solution

hydroxyl-17β-benzoate (XIb) was subjected to a mild alkaline hydrolysis followed by acetylation to afford the corresponding 2α,17β-diacetate (XVI).

The 5β and 5α configurations of 2α-hydroxyl-XIb and -XIa were further proved as follows. Oxidation of XIb and XIa with Jones reagent gave the corresponding 2-oxo derivatives, *i.e.* the previously unknown 2-oxo-5β system (XIIIb) of mp 153—154° and the previously known 2-oxo-5α system[11] (XIIIa) of mp 173.5—174° in 94.6% and 93.8% yields respectively. Microanalyses, mass spectra and other physical properties of the compounds supported their structures. Particularly the NMR spectra show singlet peaks due to the 10-methyl groups at a lower field (0.30 ppm) for XIIIb than for XIIIa supporting the 5β configuration for XIIIb.[4] Furthermore, XIIIb and XIIIa show in their ORD and CD curves negative Cotton effects with a much weaker intensity and positive Cotton effects with a stronger intensity respectively, as shown in Fig. 2. The opposite signs of Cotton effects shown by XIIIb and XIIIa[12] can well be understood by applying the Octant Rule[4,13] to the cyclohexanone system of A rings in the compounds, as visualized in the Octant projection formulae[14] XIVb for XIIIb and XIVa for XIIIa (Fig. 3).

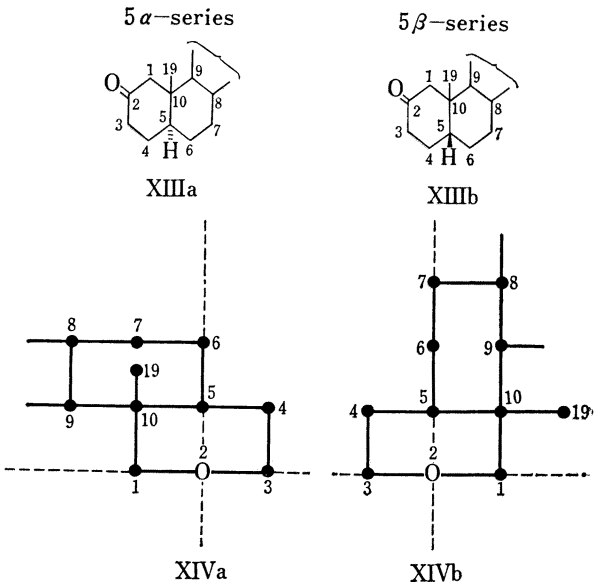


Fig. 3. Octant Projection Formulae (XIVa, XIVb) of Rings A and B of 2-Oxo-5α-(XIIIa) and -5β-(XIIIb) -steroid Series

Regarding the ORD and CD informations of the 2-oxo-5β- and -5α-steroid systems, it is now a generalized fact that the intensity of Cotton effect curves (negative sign) of the 2-oxo-5β system is extraordinarily weak compared with that of Cotton effect curves (positive sign) of the 2-oxo-5α system. The observed difference in intensities might be due to dierffent steric environments around the 2-oxo group of those compounds as visualized in their octant projection formulae XIVb and XIVa.

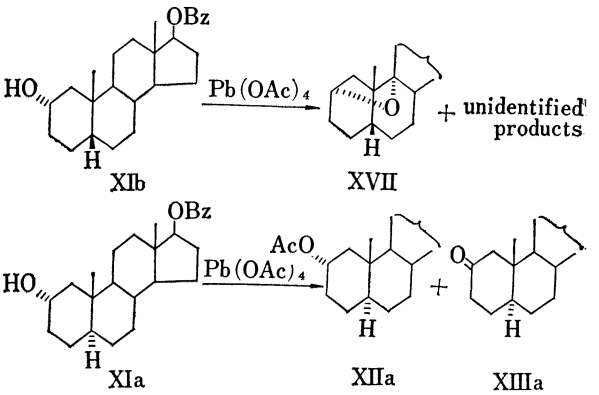


Chart 5

11) Edwards, *et al.* have reported the mp and specific rotation of the compound to be 152—156° and $[\alpha]_D$+74° (J. A. Edwards, P. G. Holton, J. C. Orr, L. C. Ibáñez, E. Necoechea, A. de la Roz, E. Segovia, R. Urguiza and A. Bowers, *J. Med. Chem.*, **6**, 174 (1963)).

12) It has been reported that 2-oxo-17β-propionyloxy-5α-androstane shows a positive sign of Cotton effect in its CD curve (K. M. Wellman, R. Records, E. Bunnenberg and C. Djerassi, *J. Am. Chem. Soc.*, **86**, 492 (1964)).

13) W. Moffit, R.B. Woodward, A. Moscowitz, W. Klyne and C. Djerassi, *J. Am. Chem. Soc.*, **83**, 4013 (1961).

14) The Octant projection formulae were derived from possible conformations of the compounds with the A or cyclohexanone ring in the preferred chair form.

Then, oxidation of XIb with lead tetraacetate (two equivs) was attempted in boiling benzene, affording the desired 17β-benzoyloxy-2α,9α-epoxy-5β-androstane (XVII) in 53.1% yield. Added to the 2α,9α-epoxide (XVII), several oily products were isolated in far less yields. However, they could not be purified by TLC. The structure of the 2α,9α-epoxide (XVII) of mp 114.5—115.5° was supported by the microanalysis and mass spectrum. Its IR spectrum shows, added to absorptions due to a benzoyloxy group in the compound, absorptions (ν 1115, 958 and 891 cm^{-1}) due to the C-O-C bond. The NMR spectrum exhibits a broad doublet due to the equatorial 2β-proton[4,10] and a singlet peak due to the 10-methyl group under a deshielding effect of the 2α,9α-epoxy function.[4] The other spectroscopic evidence of the compound supported its structure.

Oxidation of XIa, isomeric to XIb at 5C, with lead tetraacetate was carried out analogously. Epoxidation at 9C was not observed, and the only two products isolated, apart from starting material (44.3%), were the corresponding acetate (XIIa) (6.0% yield) and 2-oxo compound (XIIIa) (6.7% yield).

For further study of the 2α,9α-epoxide system, the 17β-acetoxy analogue (XIX) of 17β-benzoyloxy-2α,9α-epoxide (XVII) was used. Preparation of XIX was carried out by alkaline hydrolysis of XVII followed by acetylation. The mass and other spectroscopic evidence proved the structure of XIX to be the 17β-acetoxy analogue of XVII.

With an anticipation that acid-catalyzed epoxide fission of XIX might lead to the new synthesis of 9α-hydroxy-5β system, the epoxide XIX was treated with a mixture of acetic anhydride–boron trifluoride etherate giving two compounds, XX and XXI, in 18.0% and 71.7% yields respectively. The chromatographically less polar XX of mp 126.5—127° shows absorptions ascribable to the presence of a double bond in its UV and IR spectra. The presence of a vinylic hydrogen was denied by NMR spectroscopy, so that the location of a double bond in the compound was assumed to be 8(9) or 8(14). The appearance of signals in the NMR spectrum due to 13-(τ 9.01) and 10-methyl (τ 9.18) groups respectively, suggested the location of the double bond to be 8(14) and not 8(9).[9] The NMR spectrum further shows a multiplet assignable to the 2β-hydrogen.[15] Presence of two acetate groups in the compound was supported both by IR and NMR spectra. These evidence coupled with the microanalysis suggested the structure of XX to be 2α,17β-diacetoxy-5β-androst-8(14)-ene. Although the mass spectrum does not show its M^+ peak, it shows a fragment peak (M^+-CH_3COOH), giving another support for the structure.

Structural elucidation of the chromatographically more polar product XXI of mp 116—117° was carried out in the similar way as with XX. The microanalysis and mass spectrum supported the expected molecular formula of $C_{23}H_{34}O_4$. The compound shows absorptions due to a double bond in the UV and IR spectra respectively. The presence of a vinylic hydrogen was supported both by IR and NMR spectra. As the peaks due to the 13- and 10-methyl groups in the NMR spectrum appear at τ 9.28 and τ 8.92 respectively, the location of the double bond must be 9(11).[9] The NMR spectrum also shows a multiplet due to the equatorial 2β-proton.[4,10] The evidence suggested the structure of XXI to be 2α,17β-diacetoxy-5β-androst-9(11)-ene. The structure of the compound was further proved by the fact that catalytic hydrogenation of XXI with platinum oxide in glacial acetic acid gave XVI derived from XIb. It was therefore concluded that the transannular oxidation reaction did not cause any rearrangement or configurational change of the skeleton of XIb.

The 9(11)-eno compound (XXI) was oxidized with perbenzoic acid in chloroform to give 2α,17β-diacetoxy-9α,11α-epoxy-5β-androstane (XXII) of mp 137.5—138.5° in 92.9% yield. The microanalysis and mass spectrum supported the structure. The IR spectrum

15) The multiplet as well as that of the same 2β-hydrogen in the 9α,11α-epoxy-XXII appear at somewhat higher fields and have fairly larger half widths than those of the related compounds with 5β-configuration, XIIb, XVI, XXI and XXIV. The real reason of such anomaly is obscure.

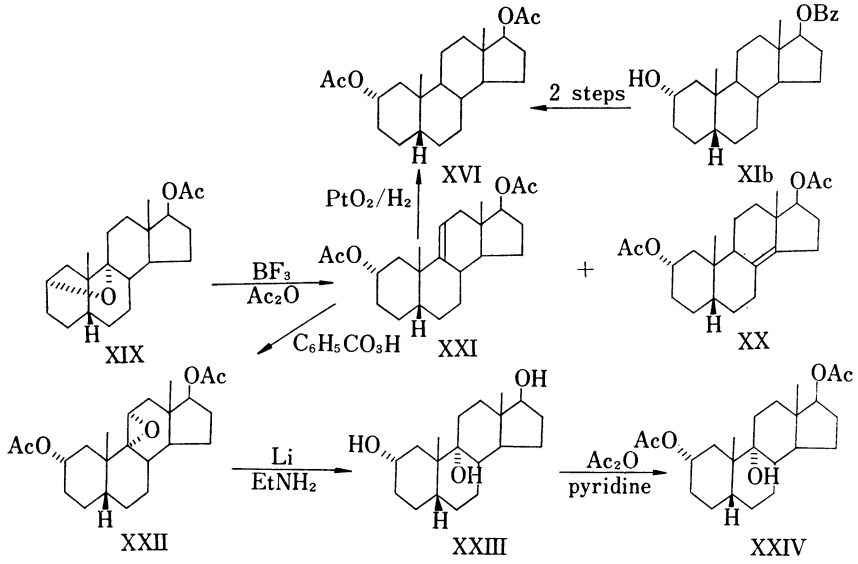


Chart 6

shows absorptions due to two acetate and the C-O-C groups. The NMR spectrum shows, in addition to a multiplet due to the 2β-proton,[15] a doublet due to the 11β-epoxide proton. The fact that the epoxy function has the α configuration was supported by NMR spectroscopy that the epoxide causes a deshielding effect toward the 10-methyl group which gave a singlet at 0.38 ppm lower field than the 13-methyl peak.[9] The other spectroscopic evidence of the compound supported its structure.

The 9α,11α-epoxide (XXII) was then treated with lithium in ethylamine which caused the reductive epoxide fission at 11C and hydrolysis of the 2α- and 17β-acetate groups affording 2α,9α,17β-trihydroxy-5β-androstane (XXIII) of mp 270—271.5° in 79.9% yield. The structure of XXIII was supported by microanalysis and mass spectrum. The presence of three hydroxyl groups in the compound was also supported by mass spectroscopy, its spectrum showing dehydrated peaks (M^+-H_2O, M^+-$2H_2O$ and M^+-$3H_2O$). Meanwhile, the compound was insoluble in chloroform and could not be subjected to NMR measurement. The triol (XXIII) was therefore subjected to acetylation with acetic anhydride in pyridine to give the diacetate (XXIV) of mp 107—108.5°. The microanalysis and mass spectrum supported the expected molecular formula of $C_{23}H_{36}O_5$. The compound shows an absorption due to a hydroxyl function in the IR spectrum. The NMR spectrum also shows a singlet peak due to a hydroxyl function which disappeared after treatment with deuterium oxide. The mass spectrum further shows dehydrated peaks (M^+-CH_3COOH-H_2O and M^+-$2CH_3COOH$-H_2O), supporting the presence of a hydroxyl and two acetate groups. These data suggested that using acetic anhydride–pyridine as reagent two hydroxyl groups of the triol (XXIII) were acetylated, however, a hydroxyl group had resisted acetylation. The hydroxyl group remained unacetylated was characterized to be a tertiary alcohol at 9C.[16] Furthermore, the NMR spectrum shows only two signals due to methine groups bearing two acetate groups, assignable to the equatorial 2β-hydrogen[4,10] and 17α-hydrogen respectively, and also a singlet peak due to the 10-methyl group under the deshielding effect of the hydroxyl function and a singlet peak due to the 13-methyl group being not influenced by the hydroxyl function.[9]

16) A. S. Hallsworth and H.B. Henbest, *J. Chem. Soc.*, **1957**, 4604.

These evidence suggested that the hydroxyl group in XXIV and then triol (XXIII) has the α configuration at 9C, and that the epoxide fission did not take place at 9C but at 11C. The informations supported the structures of XXIV and XXIII to be 2α,17β-diacetoxy-9α-hydroxy-5β-androstane and 2α,9α,17β-trihydroxy-5β-androstane respectively.

Experimental[17]

4α,5-Epoxy-17β-hydroxy-5α- (IVa) and 4β,5-Epoxy-17β-hydroxy-5β-(IVb)-androstan-3-ones——To a solution of testosterone (III) (1.0 g) in 30 ml MeOH, 5.0 ml 1N NaOH and 6.0 ml 30% H_2O_2 were successively added below 15° and the mixture was kept in the cold. The reaction was followed by TLC, and was complete in 5 hr. The reaction mixture was poured into $CHCl_3$ and the $CHCl_3$ layer was washed with water and dried (anhyd. Na_2SO_4). Concentration of the filtrate *in vacuo* gave a colorless solid product, mp 133—140°, wt. 983 mg. Repeated recrystallization from ether gave the β-epoxide (IVb) as colorless needles, mp 157—158.5°, wt. 562 mg (53.2% yield). Further recrystallization from same solvent gave sample of mp 159.5—160°. *Anal.* Calcd. for $C_{19}H_{28}O_3$: C, 74.96; H, 9.27. Found: C, 75.07; H, 9.28. $[\alpha]_D^{26}$+148.9° (c=1.17). UV λ_{max} mμ (ε): end absorption at 210 (1910), 304 (35) (). ORD (c=0.108, MeOH) $[\alpha]^{20}$ (mμ): +278° (500), +514° (400), +944° (360), +1320° (350), +2056° (340), +2194° (336) (shoulder), +2500° (326) (peak), +1361° (314), 0° (306), −945° (300), −2111° (290), −2417° (284) (trough), −2000° (270), −1306° (250), −861° (232) (peak), −917° (224). CD (c=0.108, MeOH) [θ] (mμ): 0 (349), +5209 (326), +7813 (320) (shoulder), +10789 (306) (positive maximum), +7906 (292), + 5116 (284), +372 (260), 0 (245). IR ν_{max}^{KBr} cm^{-1}: 3517 (s) (OH), 1693 (s) (C=O), 857 (s) (C–O–C). NMR τ: 6.36 (1 proton, triplet, J=8 cps) (17α-H), 7.03 (1 proton, singlet) (4α–H), 8.84 (3 protons, singlet) (19-H), 9.23 (3 protons, singlet) (18-H). Mass Spectrum m/e: 304 ($C_{19}H_{28}O_3$) (M^+).

Concentration of the ethereal mother liquor *in vacuo* gave colorless crystals, mp 140—143°, $[\alpha]_D^{20}$+42.6° (c=1.01), wt. 363 mg. The crystals were chromatographed over 180 g neutral alumina (Woelm, grade III). Elution with 400 ml 32:1 benzene–ether gave the α-epoxide (IVa) as colorless needles, mp 171.5—172.5°, wt. 128 mg (12.1% yield). Recrystallization from ether gave sample of mp 172—173°. *Anal.* Calcd. for $C_{19}H_{28}O_3$: C, 74.96; H, 9.27. Found: C, 75.05; H, 9.33. $[\alpha]^{26}$ −64.6° (c=0.94). UV λ_{max}^{KBr} mμ(ε): end absorption at 210 (3420), 300 (41) (). ORD (c=0.116, MeOH) $[\alpha]^{20}$ (mμ): −86° (500), −345° (400), −733° (365), −1250° (350), α−2200° (337) (shoulder), −2780° (324) (trough), −1638° (311), 0° (304), +1315° (298), +3426° (286), +3836° (278) (peak), +3534° (266), +2758° (245), +2672° (237) (trough), +2802° (221). CD (c=0.116, MeOH) [θ]^{20} (mμ): 0 (349), −2425 (333), −9179 (318), −13336 (306) (shoulder), −13769 (300) (negative maximum), −6754 (280), −3204 (270), −866 (255), 0 (235). IR ν_{max}^{KBr} cm^{-1}: 3449 (s) (OH), 1703 (s) (C=O), 862 (s) (C–O–C). NMR τ: 6.36 (1 proton, triplet, J=8 cps) (17α-H), 6.98 (1 proton, singlet) (4β-H), 8.93 (3 protons, singlet) (19-H), 9.23 (3 protons, singlet) (18-H). Mass Spectrum m/e: 304 ($C_{19}H_{28}O_3$) (M^+).

Further elution with 400 ml 32:1 benzene-ether gave a mixture of the α-epoxide (IVa) and its β-isomer (IVb) as colorless crystals, mp 142—146°, $[\alpha]_D^{22}$+96.8° (c=0.93), wt. 101 mg.

Further elution with 400 ml 32:1 benzene-ether gave the β-epoxide (IVb) as colorless needles, mp 156—157.5°, wt. 82 mg (7.8% yield).

The mixture of IVa and IVb (101 mg) was rechromatographed over 70 g neutral alumina (Woelm, grade III). Elution with 60 ml 19:1 benzene–ether gave the α-epoxide (IVb) as colorless needles, mp 169—171°, wt. 15 mg (1.4 % yield).

Further elution 90 ml 19:1 benzene–ether gave a mixture of IVa and IVb, mp 143—146°, $[\alpha]_D^{17}$+99.0 (c=1.00), wt. 35 mg.

Further elution with 200 ml 9:1 benzen–ether gave the β-epoxide (IVb) as colorless needles, mp 156—157°, wt. 45 mg (4.3 % yield).

Total yields of the α-epoxide (IVa) and its β-isomer (IVb) then reached 143 mg (13.5%) and 689 mg (65.3%) respectively.

17β-Acetoxy-4α,5-epoxy-5α-androstan-3-one (Va)——To a solution of IVa (200 mg) in 2.0 ml pyridine, 2.0 ml acetic anhydride was added dropwise in the cold and the mixture kept at room temperature; the

17) All melting points were taken on a Kofler-type hot plate, and are uncorrected. $[\alpha]_D$ refers to $CHCl_3$, UV absorption spectra to 95% EtOH, and IR spectra to nujol unless otherwise stated. IR and UV spectra were obtained on JASCO DS-402 G and Hitachi EPS-2U spectrophotometers, respectively. ORD and CD curves were taken using a JASCO ORD/UV-5 recorder. NMR spectra were run in $CDCl_3$ on a JEOL C-6H, Variam Associates A-60 or 100 high resolution spectrometers with tetramethylsilane as internal standard, and the intensities or peak areas were measured by the integrater. Mass spectra were determined on a JEOL JMS-O1SG high resolution mass spectrometer.

reaction was complete in 15 hr (TLC). The reaction mixture was poured into ice-water to deposit Va as colorless prisms. The prisms were filtered off, washed with dil. H_2SO_4, water, sat. $NaHCO_3$ aq. and water, and dried , mp 168.5—171°, wt. 225 mg (98.9% yield). Recrystallization from ether gave sample of mp 169.5—171.° *Anal.* Calcd. for $C_{21}H_{30}O_4$: C, 72.80; H, 8.73. Found: C, 72.99; H, 8.89. $[\alpha]_D^{22}$ −69.7° (c= 0.99). UV λ_{max} m$\mu(\varepsilon)$: end absorption at 210 (3320), 300 (40) (O=C–C(O)–). IR ν_{max} cm^{-1}: 1721 (s) and 1710—1693 (s) ($OCOCH_3$ and C=O), 826 (s) (C–O–C). NMR τ: 5.40 (1 proton, triplet, J=8 cps) (17α-H), 6.98 (1 proton, singlet) (4β-H), 7.97 (3 protons, singlet) (17β-$OCOCH_3$), 8.93 (3 protons, singlet) (19-H), 9.18 (3 protons, singlet) (18-H). Mass Spectrum m/e: 346 ($C_{21}H_{30}O_4$) (M^+).

17β-Acetoxy-4β,5-epoxy-5β-androstan-3-one (Vb)——To a solution of IVb (200 mg) in 2.0 ml pyridine, 2.0 ml acetic anhydride was added dropwise in the cold and the reaction mixture kept at room temperature. The reaction was followed by TLC and was complete in 14 hr. The reaction mixture was poured into ice-water to deposit Vb as colorless needles. The needles were filtered off, washed with dil. H_2SO_4, water, sat. $HaHCO_3$ aq. and water, and dried, mp 159—160.5°, wt. 223 mg (98.0 % yield). Recrystallization from ether gave sample of mp 160.5—161.5°. *Anal.* Calcd. for $C_{21}H_{30}O_4$: C, 72.80; H, 8.73. Found: C, 73.93; H, 8.85. $[\alpha]_D^{20}$+133.5° (c=1.07). UV λ_{max} m$\mu(\varepsilon)$: end absorption at 210 (2130), 304 (34) (O=C–C(O)–). IR ν_{max} cm^{-1}: 1728 (s), 1713 (s) and 1698 (shoulder) ($OCOCH_3$ and C–O), 862 (s) (C–O–C). NMR τ: 5.40 (1 proton, triplet, J=8 cps) (17α-H), 7.03 (1 proton, singlet) (4α-H), 7.98 (3 protons, singlet) (17β-$OCOCH_3$), 8.84 (3 protons, singlet) (19-H), 9.18 (3 protons, singlet) (18-H). Mass Spectrum m/e: 346 ($C_{21}H_{30}O_4$) (M^+).

17β-Benzoyloxy-4α,5-epoxy-5α-androstan-3-one (VIa)——To a solution of IVa (200 mg) in 2.0 ml pyridine, 111 mg benzoyl chloride was added dropwise in the cold and the reaction mixture kept at room temperature; the reaction was complete in 2 hr (TLC). The reaction mixture was poured into ice–water to deposit VIa as colorless needles. The needles were filtered off, washed with dil. H_2SO_4, water, sat. $NaHCO_3$ aq. and water, and dried, mp 169—171°, wt. 265 mg (98.9%) yield. Recrystallization from ether gave sample of mp 170.5—171.5°. *Anal.* Calcd. for $C_{26}H_{32}O_4$: C, 76.44; H, 7.90. Found: C, 76.51; H, 8.19. $[\alpha]_D^{22}$ −16.5° (c=1.05). UV λ_{max} m$\mu(\varepsilon)$: 230 (14320) ($OCOC_6H_5$), 300 (shoulder) (42) (O=C–C(O)–). IR ν_{max} cm^{-1}: 3061 (w) (arom. C–H), 1711 (s), 1705 (s) and 1696 (shoulder) ($OCOC_6H_5$ and C=O), 1601 (m) and 1583 (m) (arom. C=C), 869 (m) (C-O-C), 721 (s) (-C_6H_5). NMR τ: 1.96 (2 protons, multiplet) and 2.50 (3 protons, multiplet) (17β-$OCOC_6H_5$), 5.15 (1 proton, triplet, J=8 cps) (17α-H), 6.97 (1 proton, singlet) (4β-H), 8.93 (3 protons, singlet) (19-H), 9.04 (3 protons, singlet) (18-H). Mass Spectrum m/e: 408 ($C_{26}H_{32}O_4$) (M^+).

17β-Benzoyloxy-4β,5-epoxy-5β-androstan-3-one (VIb)——To a solution of IVb (5.0 g) in 50 ml pyridine, 2.77 g benzoyl chloride was added dropwise in the cold and the mixture kept at room temperature; the reaction was complete in 50 min (TLC). The reaction mixture was poured into ice–water to deposit VIb as colorless needles. The needles were filtered off, washed with dil. HCl, water, sat. $NaHCO_3$ aq and water, and dried, mp 174—177.5°, wt. 6.698 g (99.8% yield). Recrystallization from ether gave sample of mp mp 177—178°. *Anal.* Calcd. for $C_{26}H_{32}O_4$: C, 76.44; H, 7.90. Found: C, 76.28; H, 8.17. $[\alpha]_D^{31}$+183.0° (c=0.47). UV λ_{max} mμ (ε): 230 (14930) ($OCOC_6H_5$), 304 (35) (shoulder) (O=C–C(O)–). IR ν_{max} cm^{-1}: 3086 (w), 3060 (w) and 3036 (w) (arom. C–H), 1712 (s) and 1699 (shoulder) ($OCOC_6H_5$ and C=O), 1603 (m) and 1585 (m) (arom. C=C), 863 (s) (C-O-C), 718 (s) (-C_6H_5). NMR τ: 1.96 (2 protons, multiplet) and 2.50 (3 protons, multiplet) (17β-$OCOC_6H_5$), 5.16 (1 proton, triplet, J=8 cps) (17α-H), 7.02 (1 proton, singlet) (4α-H), 8.83 (3 protons, singlet) (19-H), 9.04 (3 protons, singlet) (18-H). Mass Spectrum m/e: 408 ($C_{26}H_{32}O_4$) (M^+).

Abnormal Ring Opening of VIb with dil. H_2SO_4 as a Catalyst: Formation of 17β-Benzoyloxy-2α-hydroxyandrost-4-en-3-one (VII)——To a solution of VIb (4.0 g) in 160 ml acetone, a mixture of 2.0 ml conc. H_2SO_4 and 6.0 ml water was added dropwise and the temperature of the mixture was maintained at 35°. The reaction was followed by TLC, and was complete in 32 hr. The reaction mixture was poured into ice–water to deposit colorless crystals. The crystals were filtered off and washed with water, and dried, mp 173—178°, wt. 3.730 g. They were chromatographed over 112 g silica gel (Kanto Chemical Co.). Elution with 1250 ml 32: 1 benzene–ether gave VII as colorless needles, mp 196—199°, wt. 3.436 g (85.9% yield). Recrystallization from MeOH gave sample of mp 199—201.5°. *Anal.* Calcd. for $C_{26}H_{32}O_4$: C, 76.44; H, 7.90. Found: C, 76.28; H, 8.05. $[\alpha]_D^{31}$ +180.9° (c=0.68). UV λ_{max} m$\mu(\varepsilon)$: 234 (26050) ($OCOC_6H_5$ and $O=C_3-C_4=C_5-$). IR ν_{max} cm^{-1}: 3490 (m) (OH), 3078 (w), 3055 (w) and 3026 (w) (arom. C–H and H>C=C–), 1713 (s) ($OCOC_6H_5$), 1675 (s) (C=O), 1616 (s) (C=C), 1599 (m) amd 1582 (m) (arom. C=C), 720 (s) (-C_6H_5). NMR τ: 1.96 (2 protons, multiplet) and 2.50 (3 protons, multiplet) (17β-$OCOC_6H_5$), 4.20 (1 proton, singlet) (4-H), 5.15 (1 proton, triplet, J=8 cps) (17α-H), 5.74 (1 proton, quartet, $J_{2\beta\text{-}1\alpha}$=14 cps, $J_{2\beta\text{-}1\beta}$=6 cps) (2β-H), 6.41 (1 proton, doublet, J=2 cps) (2α-OH), 8.67 (3 protons, singlet) (19-H), 9.01 (3 protons, singlet) (18-H). Mass Spectrum m/e: 408 ($C_{26}H_{32}O_4$) (M^+).

17β-Benzoyloxy-2α-hydroxyandrost-4-en-3-one Ethylenethioketal (VIII)——To a solution of VII (7.0 g) in 220 ml glacial acetic acid, 10.6 ml ethanedithiol and 10.6 ml BF_3·etherate were successively added and the

mixture kept at room temperature for 40 min when colorless plates began to precipitate. The reaction was complete in 1 hr (TLC). The reaction mixture was diluted with 50 ml MeOH and then 50 ml water, poured into ice–water, and the deposited VIII as colorless plates were filtered off, washed with water, and dried, mp 234—238°, wt. 8.30 g (99.9% yield, one spot on TLC). Recrystallization from acetone gave sample of mp 243—245°, wt. 6.55 g (78.9% yield). Further recrystallization from same solvent gave sample of mp 245.5—246.5°. *Anal.* Calcd. for $C_{28}H_{36}O_3S_2$: C, 69.38; H, 7.49; S, 13.23. Found: C, 69.51; H, 7.61; S, 13.30. $[\alpha]_D^{31}+196.9°$ ($c=0.66$). UV λ_{max} m$\mu(\varepsilon)$: end absorption at 210 (14540), 227 (18480). IR ν_{max} cm^{-1}: 3448 (m) (OH), 3078 (w), 3058 (w) and 3026 (w) (arom. C–H and $_H$>C=C<), 1716 (s) ($OCOC_6H_5$), 1646 (w) (C=C), 1603 (m) and 1581 (m) (arom. C=C),711 (s) ($-C_6H_5$). NMR τ: 1.97 (2 protons, multiplet) and 2.51 (3 protons, multiplet) (17β-$OCOC_6H_5$), 4.50 (1 proton, singlet) (4-H), 5.16 (1 proton, triplet, $J=8$ cps) (17α-H), 6.03 (1 proton, multiplet, half width=23 cps) (2β-H), 6.63 (4 protons, triplet, $J=2.7$ cps) (-S-C**H**$_2$-C**H**$_2$-S-), 8.88 (3 protons, singlet) (19-H), 9.05 (3 protons, singlet) (18-H). Mass Spectrum *m/e*: 484 ($C_{28}H_{36}O_3S_2$) (M^+).

17β-Benzoyloxy-2α-hydroxyandrost-4-ene (IX)——To a solution of VIII (500 mg) in 110 ml EtOH, *ca.* 15 g Raney Ni, prepared according to the literature[18] and deactivated by refluxing in AcOEt and acetone for 15 min each, was added and the suspension was refluxed for 8 min. Concentration of the filtrate *in vacuo* gave an oily product, wt. 413 mg. This was chromatographed over 41.3 g silica gel (Kanto Chemical Co.). Elution with 1100 ml 32: 1 benzene–ether gave IX as a colorless non-crystalline solid, mp 76—83°, wt. 398 mg (97.8% yield). The compound resisted crystallization, however, was proved to be homogeneous by TLC. IR ν_{max} cm^{-1}: 3351 (s) (OH), 3076 (w), 3056 (w) and 3026 (w) (arom. C–H and $_H$>C=C<), 1712 (s) ($OCOC_6H_5$), 1649 (w) (C=C), 1600 (m) and 1585 (m) (arom. C=C), 715 (s) ($-C_6H_5$). NMR τ: 1.96 (2 protons, multiplet) and 2.50 (3 protons, multiplet) (17β-$OCOC_6H_5$), 4.81 (1 proton, multiplet) (4-H), 5.15 (1 proton, triplet, $J=8$ cps) (17α-H), 6.14 (1 proton, multiplet, half width=23 cps) (2β-H), 8.89 (3 protons, singlet) (19-H), 9.04 (3 protons, singlet) (18-H).

2α-Acetoxy-17β-benzoyloxyandrost-4-ene (X)——To a solution of IX (177 mg) in 1.8 ml pyridine, 1.0 ml acetic anhydride was added dropwise in the cold and the mixture kept at room temperature; the reaction was complete in 3 hr (TLC). The reaction mixture was poured into ice–water to deposit X as colorless needles. The needles were filtered off, washed with dil. HCl, water, sat. $NaHCO_3$ aq and water, and dried, mp 134—144°, wt. 194 mg (99.0% yield, one spot on TLC). Recrystallization from MeOH gave sample of mp 147—148°, wt. 174 mg (88.8% yield). Further recrystallization from same solvent gave sample of mp 152—153.5°. *Anal.* Calcd. for $C_{28}H_{36}O_4$: C, 77.03; H, 8.31. Found: C, 76.94; H, 8.38. $[\alpha]_D^{22}+68.1°$ ($c=0.96$). UV λ_{max} m$\mu(\varepsilon)$: end absorption at 210 (7340), 230 (15100) ($OCOC_6H_5$). IR ν_{max} cm^{-1}: 3078 (w), 3057 (w) and 3028 (w) (arom. C–H and $_H$>C=C<), 1737 (shoulder) and 1721 (s) ($OCOCH_3$ and $OCOC_6H_5$), 1647 (w) (C=C), 1605 (m) and 1583 (m) (arom. C=C), 712 (s) ($-C_6H_5$). NMR τ: 1.96 (2 protons, multiplet) and 2.50 (3 protons, multiplet) (17β-$OCOC_6H_5$), 4.83 (1 proton, multiplet) (4-H), 5.16 (1 proton, multiplet, half width=23 cps) (2β-H), 5.16 (1 proton, triplet, $J=8$ cps) (17α-H), 7.98 (3 protons, singlet) (2α-$OCOCH_3$), 8.88 (3 protons, singlet) (19-H), 9.04 (3 protons, singlet) (18-H). Mass Spectrum *m/e*: 376 ($C_{26}H_{32}O_2$) (M^+–CH_3COOH).

Catalytic Hydrogenation of IX: Formation of 17β-Benzoyloxy-2α-hydroxy-5α- (XIa) and -5β- (XIb) -androstanes——IX (1.0 g) in 50 ml 99% EtOH was hydrogenated with 500 mg 20% Pt-C as catalyst at 4°. After absorption of hydrogen ceased, the catalyst was filtered off, and the filtrate was concentrated *in vacuo* to give a colorless oily product, wt. 986 mg. This was chromatographed over 200 g silica gel (Kanto Chemical Co.). Elution with 2000 ml benzene gave colorless needles, mp 72—88°, wt. 116 mg. They showed one spot on TLC. IR ν_{max} cm^{-1}: 3081 (w) and 3051 (w) (arom. C–H), 1712 (s) ($OCOC_6H_5$), 1601 (m) and 1588 (m) (arom. C=C), 714 (s) ($-C_6H_5$), no hydroxyl absorption. They were supposed to be 17β-benzoyloxyandrostane, however, further confirmation of the structure was not carried out.

Further elution with 1700 ml 49:1 benzene–ether gave XIb as colorless needles, mp 142—144°, wt. 324mg (32.2 % yield). Recrystallization from MeOH gave sample of mp 144—145°. *Anal.* Calcd. for $C_{26}H_{36}O_3$: C, 78.74; H, 9.15. Found: C, 78.45; H, 9.26. $[\alpha]_D^{24}+54.7°$ ($c=0.75$). UV λ_{max} m$\mu(\varepsilon)$: 230 (14270) ($OCOC_6H_5$). IR ν_{max} cm^{-1}: 3525 (s) (OH), 3076 (w) and 3058 (w) (arom. C-H), 1693 (s) ($OCOC_6H_5$), 1601 (m) and 1583 (m) (arom. C=C), 726 (s) ($-C_6H_5$). NMR τ: 1.96 (2 protons, multiplet) and 2.50 (3 protons, multiplet) (17β-$OCOC_6H_5$), 5.16 (1 proton, triplet, $J=8$ cps) (17α-H), 5.94 (1 proton, multiplet, half width=7 cps) (2β-H), 9.06 (6 protons, singlet) (18- and 19-H). Mass Spectrum *m/e*: 396 ($C_{26}H_{36}O_3$) (M^+).

Further elution with 900 ml 49: 1 benzene–ether gave XIa as colorless needles, mp 168—171°, wt. 170 mg (16.9 % yield, one spot on TLC). Recrystallization from MeOH gave sample of mp 172—174°, wt. 122 mg (12.1 % yield). Further recrystallization from same solvent gave sample of mp 175.5—176.7°. *Anal.* Calcd. for $C_{26}H_{36}O_3$: C, 78.74; H, 9.15. Found: C, 78.48; H, 9.08. $[\alpha]_D^{24}+60.5°$ ($c=0.86$). UV λ_{max} m$\mu(\varepsilon)$; 230 (14890) ($OCOC_6H_5$). IR ν_{max} cm^{-1}: 3590 (m), 3500 (s) and 3450 (s) (OH), 3080 (w) and 3058 (w) (arom. C–H), 1712 (s) and 1700 (s) ($OCOC_6H_5$), 1602 (m) and 1583 (m) (arom. C=C), 715 (s) ($-C_6H_5$). NMR τ: 1.96 (2 protons, multiplet) and 2.50 (3 protons, multiplet) (17β-$OCOC_6H_5$), 5.16 (1 proton, triplet, $J=8$ cps) (17α-H),

18) R. Mozingo, "Organic Syntheses," Coll. Vol. III, ed. by E.C. Horning, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 181.

6.26 (1 proton, multiplet, half width=23 cps) (2β-H), 6.54 (1 proton, singlet) (2α-OH), 9.08 (3 protons, singlet) (18-H), 9.18 (3 protons, singlet) (19-H). Mass Spectrum *m/e*: 396 ($C_{26}H_{36}O_3$) (M^+).

2α-Acetoxy-17β-benzoyloxy-5α-androstane (XIIa)——To a solution of XIa (100 mg) in 1.5 ml pyridine, 1.5 ml acetic anhydride was added dropwise in the cold and the mixture kept at room temperature. The reaction was followed by TLC , and was complete in 8 hr. The reaction mixture was poured into ice-water to deposit XIIa as colorless needles. The needles were filtered off, washed with dil. H_2SO_4, water, sat. $NaHCO_3$ aq and water, and dried, mp 199.5—202°, wt. 110 mg (99.4% yield). Recrystallization from MeOH gave sample of mp 202—203.5°. *Anal.* Calcd. for $C_{28}H_{38}O_4$: C, 76.67; H, 8.73. Found: C, 76.56; H, 8.99. $[\alpha]_D^{24}$ +23.0° (*c*=1.00). UV λ_{max} mμ(ε): 230 (14600) ($OCOC_6H_5$). IR ν_{max} cm^{-1}: 3073 (w) and 3058 (w) (arom. C–H), 1735 (shoulder), 1728 (s) and 1720 (s) ($OCOCH_3$ and $OCOC_6H_5$), 1602 (m) and 1585 (m) (arom. C=C), 712 (s) ($-C_6H_5$). NMR τ: 1.96 (2 protons, multiplet) and 2.50 (3 protons, multiplet) (17β-$OCOC_6H_5$), 5.16 (1 proton, multiplet, half width=23 cps) (2β-H), 5.16 (1 proton, triplet, *J*=8 cps) (17α-H), 8.01 (3 protons, singlet) (2α-$OCOCH_3$), 9.08 (3 protons, singlet) (18-H), 9.14 (3 protons, singlet) (19-H). Mass Spectrum *m/e*: 438 ($C_{28}H_{38}O_4$) (M^+).

2α-Acetoxy-17β-benzoyloxy-5β-androstane (XIIb)——To a solution of XIb (100 mg) in 1.5 ml pyridine, 1.5 ml acetic anhydride was added dropwise in the cold and the mixture kept at room temperature. The reaction was followed by TLC, and was complete in 75 hr. The reaction mixture was poured into ice-water to deposit XIIb as colorless needles. The needles were filtered off, washed with dil. H_2SO_4, water, sat. $NaHCO_3$ aq and water, and dried, mp 156—157.5°, wt. 108 mg (97.6% yield). Recrystallization from MeOH gave sample of mp 158.5—159.5°. *Anal.* Calcd. for $C_{28}H_{38}O_4$: C, 76.67; H, 8.73. Found: C, 76.44; H, 8.67. $[\alpha]_D^{25}$ +39.3° (*c*=1.03). UV λ_{max} mμ(ε): 230 (14310) ($OCOC_6H_5$). IR ν_{max} cm^{-1}: 3085 (w), 3058 (w) and 3030 (w) (arom. C-H), 1736 (shoulder), 1728 (s) and 1717 (s) ($OCOCH_3$ and $OCOC_6H_5$), 1606 (m) and 1586 (m) (arom. C=C), 715(s) ($-C_6H_5$). NMR τ: 1.95 (2 protons, multiplet) and 2.49 (3 protons, multiplet) (17β-$OCOC_6H_5$), 5.00 (1 proton, multiplet, half width=7 cps) (2β-H), 5.15 (1 proton, triplet, *J*=8 cps) (17α-H), 8.00 (3 protons, singlet) (2α-$OCOCH_3$), 9.06 (3 protons, singlet) (19-H) 9.08 (3 protons, singlet) (18-H). Mass Spectrum *m/e*: 438 ($C_{28}H_{38}O_4$) (M^+).

17β-Benzoyloxy-2-oxo-5α-androstane (XIIIa)——To a stirred solution of XIa (120 mg) in 18 ml acetone, 0.24 ml Jones reagent[19] was added dropwise; the temperature of the mixture was maintained at 23°. The reaction was complete in 10 min (TLC), when the browny reaction mixture was diluted with water to deposit colorless crystals. The crystals were extracted into $CHCl_3$. The $CHCl_3$ layer was washed with sat. $NaHCO_3$ aq and water, and dried (anhyd. Na_2SO_4). Concentration of the filtrate *in vacuo* gave colorless crystals, mp 171—173°, wt. 118 mg. They were chromatographed over 12 g silica gel (Kanto Chemical Co.). Elution with 380 ml benzene gave XIIIa as colorless needles, mp 173—173.5°, wt. 112 mg (93.8% yield). Recrystallization from EtOH gave sample of mp 173.5—174°. *Anal.* Calcd. for $C_{26}H_{34}O_3$: C, 79.15; H, 8.69. Found: 78.99; H, 8.62. $[\alpha]_D^{20}$ +87.3° (*c*=0.126, MeOH). ORD (*c*=0.126, MeOH) $[\alpha]^{20}$ (mμ): +159° (500), 246° (400), +436°(350), +674°(329), +992°(320), 1206°(314) (shoulder), +1397°(307) (peak), +1198°(300), +587° (290), 0° (283), −294° (276), −540° (268) (trough), −246° (255). CD (*c*=0.126, MeOH) $[\theta]^{20}$ (mμ): 0 (326), +2945 (308), +4702 (304), +5683 (300), +6923 (295) (shoulder), +7130 (290), +7388 (285) (positive maximum), +6096 (281), +3875 (273), +1188 (255). UV λ_{max} mμ(ε): 230 (14990) ($OCOC_6H_5$). IR ν_{max} cm^{-1}: 3059 (w) (arom. C–H), 1720 (shoulder), 1713 (s) and 1699 (shoulder) (C=O and $OCOC_6H_5$), 1600 (m) and 1582 (m) (arom. C=C), 720 (s) ($-C_6H_5$). NMR τ: 1.95 (2 protons, multiplet) and 2.50 (3 protons, multiplet) (17β-$OCOC_6H_5$), 5.16 (1 proton, triplet, *J*=8 cps) (17α-H), 9.05 (3 protons, singlet) (18-H), 9.21 (3 protons, singlet) (19-H). Mass Spectrum *m/e*: 394 ($C_{26}H_{34}O_3$) (M^+).

17β-Benzoyloxy-2-oxo-5β-androstane (XIIIb)——To a stirred solution of XIb (120 mg) in 18 ml acetone, 0.24 ml Jones reagent[19] was added dropwise; the temperature of the mixture was maintained at 16°. The reaction was complete in 10 min (TLC), when the browny reaction mixture was diluted with water to deposit colorless crystals. The crystals were extracted into $CHCl_3$ and the $CHCl_3$ layer was washed with sat. $NaHCO_3$ aq and water, and dried (anhyd. Na_2SO_4). Concentration of the filtrate *in vacuo* gave colorless needles, mp 146—149.5°, wt. 119 mg. They were chromatographed over 12 g silica gel (Kanto Chemical Co.). Elution with 340 ml benzene gave XIIIb as colorless needles, mp 151—151.5°, wt. 113 mg (94.6% yield). Recrystallization from MeOH gave sample of mp 153—154°. *Anal.* Calcd. for $C_{26}H_{34}O_3$: C, 79.15; H, 8.69. Found: C, 79.04; H, 8.72. $[\alpha]_D^{19}$ +53.6° (*c*=0.112, MeOH). ORD (*c*=0.112, MeOH) $[\alpha]^{19}$ (mμ): +71° (500), +94° (420), +134° (400), +210° (350), +223° (335), +223° (329) (peak), +223° (327), +156° (317) (shoulder), +147° (311), 143° (307) (trough), +281° (300), +567° (291), +906° (286). CD (*c*=0.112, MeOH) $[\theta]^{19}$ (mμ): 0 (325), −407 (314), −872 (308), −1337 (305), −1628 (303) (shoulder), −2267 (295), −2325 (291) (negative maximum), −1860 (286), −930 (280), −581 (275). UV λ_{max} mμ (ε): 230 (14670) ($OCOC_6H_5$). IR ν_{max} cm^{-1}: 3087 (w), 3060 (w) and 3040 (w) (arom. C–H), 1722 (shoulder) and 1712 (s) (C=O and $OCOC_6H_5$), 1602 (m) and 1582 (m) (arom. C=C), 729 (s) ($-C_6H_5$). NMR τ: 1.97 (2 protons, multiplet) and 2.51 (3 protons, multiplet) (17β-$OCOC_6H_5$), 5.21 (1 proton, triplet, *J*=8 cps) (17α-H), 8.91 (3 protons, singlet) (19-H), 9.08 (3 protons, singlet) (18-H). Mass Spectrum *m/e* : 394 ($C_{26}H_{34}O_3$) (M^+).

19) K. Bowden, I.M. Heilbron, E.R.H. Jones and B.C.L. Weedon, *J. Chem. Soc.*, **1946**, 39; P. Bladon, J. M. Fabian, H. B. Henbest, H.P. Koch and G. W. Wood, *ibid.*, **1951**, 2407.

2α,17β-Diacetoxy-5β-androstane (XVI)——To a solution of XIb (50 mg, 0.126 m moles) in 180 ml MeOH, a mixture of 200 mg (2.38 m moles) $NaHCO_3$ and 20 ml water was added, and the mixture was refluxed for 48 hr (TLC). The reaction mixture was concentrated *in vacuo* followed by addition of water to deposit colorless crystals. The crystals were extracted into ether and the ethereal layer was washed with water and dried (anhyd. Na_2SO_4). Concentration of the filtrate *in vacuo* gave colorless needles, mp 185—192°, wt. 36 mg. The crystals were chromatographed over 3.6 g silica gel (Kanto Chemical Co.). Elution with 90 ml 4: 1 benzene–ether gave **2α,17β-dihydroxy-5β-androstane** (XV) as colorless needles, mp 195—196°, wt. 34 mg (92.3% yield, one spot on TLC). IR ν_{max} cm^{-1}: 3581 (w) and 3356 (s) (2α- and 17β-OH). UV λ_{max}: transparent above 210 mμ. The compound was subjected to acetylation without further purification.

To a solution of XV (25 mg) in 0.7 ml pyridine, 0.3 ml acetic anhydride was added dropwise in the cold and the mixture kept at room temperature; the reaction was complete in 120 hr (TLC). The reaction mixture was poured into ice–water to deposit a colorless oily product which was extracted into ether. The ethereal layer was washed with dil. H_2SO_4, water, sat. $NaHCO_3$ aq and water, and dried (anhyd. Na_2SO_4). Concentration of the filtrate *in vacuo* gave colorless crystals, mp 120—123°, wt. 32 mg. They were chromatographed over 3.2 g silica gel (Kanto Chemical Co.). Elution with 240 ml 1:4 pet. ether–benzene gave the 2α,17β-diacetate (XVI) as colorless needles, mp 123—125°, wt. 29 mg (90.1% yield). Recrystallization from MeOH gave sample of mp 125—126°. *Anal.* Calcd. for $C_{23}H_{36}O_4$: C, 73.36; H, 9.64. Found: C, 73.52; H, 9.87. $[\alpha]_D^{20}$ −5.0° (c=1.00). UV λ_{max} mμ(ε): end absorption at 210 (137). IR ν_{max} cm^{-1}: 1737 (s) and 1729 (s) (2α- and 17β-$OCOCH_3$). NMR τ: 4.99 (1 proton, multiplet, half width=8 cps) (2β-H), 5.41 (1 proton, triplet, J=8 cps) (17α-H), 7.98 (3 protons, singlet) (17β-$OCOCH_3$), 8.01 (3 protons, singlet) (2α-$OCOCH_3$), 9.07 (3 protons, singlet) (19-H), 9.23 (3 protons, singlet) (18-H). Mass Spectrum m/e: 376 ($C_{23}H_{36}O_4$) (M^+).

Transannular Cyclization Reaction of XIb with Lead Tetraacetate: Formation of 17β-Benzoyloxy-2α,-9α-epoxy-5β-androstane (XVII)——To a solution of XIb (700 mg, 1.77 m moles) in 16 ml anhydrous benzene, 1.582 g (3.57 m moles) lead tetraacetate was added, and the mixture refluxed for 5 min when a colorless solid began to precipitate. The reaction was followed by TLC, and was complete in 4 hr. After cooling, the reaction mixture was diluted with ether and washed with water when a brown solid precipitated. The ethereal layer was separated, dried (anhyd. Na_2SO_4), and concentrated *in vacuo* to give a yellow oily residue, wt. 824 mg. This was chromatographed over 412 g silica gel (Kanto Chemical Co.). Elution with 1500 ml 99:1 benzene–ether gave XVII as colorless prisms, mp 114—115.3°, wt. 370 mg (53.1% yield). Recrystallization from MeOH gave sample of mp 114.5—115.5°. *Anal.* Calcd. for $C_{26}H_{34}O_3$: C, 79.15; H, 8.69. Found: C, 78.87; H, 8.58. $[\alpha]_D^{26}$+17.9° (c=1.01). UV λ_{max} mμ(ε): 230 (13400) ($OCOC_6H_5$). IR ν_{max} cm^{-1}: 3052 (w) and 3028 (w) (arom. C-H), 1712 (s) ($OCOC_6H_5$), 1601 (m) and 1582 (m) (arom. C=C), 1115 (s), 958 (s) and 891 (s) (C-O-C), 733 (s) (-C_6H_5). NMR τ: 1.96 (2 protons, multiplet) and 2.50 (3 protons, multiplet) (17β-$OCOC_6H_5$), 5.05 (1 proton, triplet, J=8 cps) (17α-H), 5.81 (1 proton, doublet, J=7 cps) (2β-H), 8.95 (3 protons, multiplet) (19-H), 9.05 (3 protons, singlet) (18-H). Mass Spectrum m/e: 394 ($C_{26}H_{34}O_3$) (M^+).

Further elution with 600 ml 99: 1 benzene–ether gave a colorless oily product, wt. 97 mg, which gave two spots on TLC. Attempt of purification of the compound by TLC was unsuccessful and further confirmation of the structure was not carried out.

Further elution with 400 ml 99: 1 benzene–ether gave a colorless oily product, wt. 37 mg, which showed two spots on TLC. Attempt of purification of the compound by TLC was uncuccessful and further confirmation of the structure was not carried out.

Further elution with 700 ml 49: 1 benzene–ether gave a colorless oily product, wt. 16 mg, which gave two spots on TLC. Attempt of purification of the compound by TLC was unsuccessful and further confirmation of the structure was not carried out.

Treatment of XIa with Lead Tetraacetate: Formation of XIIa and XIIIa——To a solution of XIa (300 mg, 0.76 m moles) in 6.8 ml anhydrous benzene, 678 mg (1.53 m moles) lead tetraacetate was added, and the mixture refluxed for 3 min when a brown solid began to precipitate. The mixture continued to reflux for 4 hr. After cooling, the reaction mixture was diluted with ether and washed with water when a brown solid precipitated. The ethereal layer was separated, dried (anhyd. Na_2SO_4), and concentrated *in vacuo* to give a yellow oily residue, wt. 345 mg. This was chromatographed over 173 g silica gel (Kanto Chemical Co.). Elution with 600 ml 1: 4 pet. ether–benzene gave XIIa as colorless prisms, mp 197.5—199.5°, wt. 20 mg (6.0 % yield). Recrystallization from MeOH gave sample of mp 201—201.5°, alone and on admixture with a sample of XIIa. Their IR spectra were superposable, IR ν_{max} cm^{-1}: 3076 (w) and 3058 (w) (arom. C–H), 1736 (shoulder), 1728 (s) and 1720 (s) ($OCOCH_3$ and $OCOC_6H_5$), 1602 (m) and 1585 (m) (arom. C=C), 720 (s) (-C_6H_5).

Further elution with 360 ml 49: 1 benzene–ether gave XIIIa as colorless needles, mp 168—170.5°, wt. 20 mg (6.7 % yield). Recrystallization from MeOH gave sample of mp 171.5—173°, alone and on admixture with a sample of XIIIa. Their IR spectra were superposable, IR ν_{max} cm^{-1}: 3064 (w) and 3038 (w) (arom. C-H), 1720 (s), 1712 (s), 1705 (s) and 1697 (s) (C=O and $OCOC_6H_5$), 1600 (m) and 1582 (m) (arom. C=C), 720 (s) (-C_6H_5).

Further elution with 180 ml 24: 1 benzene–ether gave XIa of colorless prisms as the recovered starting material, mp 168.5—171.5°, wt. 133 mg (44.3 % yield). Recrystallization from MeOH gave sample of mp 174.5—175.5°, alone and on admixture with a sample of XIa. Their IR spectra were superposable, IR ν_{max}

cm^{-1}. 3594 (m), 3501 (s) and 3450 (s) (OH), 3086 (w) and 3058 (w) (arom. C–H), 1713 (s) and 1700 (s) ($OCOC_6H_5$), 1602 (m) and 1583 (m) (arom. C=C), 714 (s) ($-C_6H_5$).

17β-Acetoxy-2α,9α-epoxy-5β-androstane (XIX)——To a solution of XVII (596 mg, 1.51 m moles) in 120 ml MeOH, 3.0 ml aqueous solution of potassium hydroxide (containing 1.02 g or 18.2 mmoles of KOH) was added, and the mixture was refluxed. The reaction was followed by TLC, and was complete in 9 hr. The reaction mixture was concentrated *in vacuo* to give colorless needles. They were extracted into ether, washed with water, and dried (anhyd. Na_2SO_4). Concentration of the filtrate *in vacuo* gave 2α,9α-epoxy-17β-hydroxy-5β-androstane (XVIII) as colorless prisms, mp 169—170°, wt. 432 mg (98.5% yield, one spot on TLC). UV λ_{max}: transparent above 210 mμ. IR ν_{max} cm^{-1}: 3429 (s) (OH), 1102 (s), 952(s) and 887 (s) (C–O–C). This was subjected to acetylation without further purification.

To a solution of XVIII (548 mg) in 11.0 ml pyridine, 11.0 ml acetic anhydride was added dropwise in the cold and the mixture kept at room temperature; the reaction was complete in 16 hr (TLC). The reaction mixture was poured into ice-water to deposit colorless crystals which were extracted into ether. The ethereal layer was washed with dil. H_2SO_4, water, sat. $NaHCO_3$ aq and water, and dried (anhyd. Na_2SO_4). Concentration of the filtrate *in vacuo* gave the 17β-acetate (XIX) as colorless plates, mp 97—98.5°, wt. 626 mg (99.8% yield). Recrystallization from MeOH gave sample of mp 99—99.5°. *Anal.* Calcd. for $C_{21}H_{32}O_3$: C, 75.86; H, 9.70. Found: C, 76.02; H, 9.70. $[\alpha]_D^{24}$ −29.1° (*c*=1.00). UV λ_{max} mμ (ε): end absorption at 210 (80). IR ν_{max} cm^{-1}: 1738 (s) ($OCOCH_3$), 1103 (s), 970 (s) and 889 (s) (C-O-C). NMR τ: 5.30 (1 proton, triplet, J=8 cps) (17α-H), 5.83 (1 proton, doublet, J=7 cps) (2β-H), 7.99 (3 protons, singlet) (17β-$OCOCH_3$), 8.95 (3 protons, singlet) (19-H), 9.19 (3 protons, singlet) (18-H). Mass Spectrum *m/e*: 332 ($C_{21}H_{32}O_3$) (M^+).

Ring Opening of XIX with Acetic Anhydride–Boron Trifluoride Etherate: Formation of 2α,17β-Diacetoxy-5β-androst-8(14)-ene (XX) and 2α,17β-Diacetoxy-5β-androst-9(11)-ene (XXI)——To a solution of XIX (552 mg, 1.66 mmoles) in 1.4 ml anhyd. benzene, a mixture of 6.02 ml acetic anhydride and 0.11 ml (0.871 mmoles) boron trifluoride etherate was added and the reaction mixture kept at room temperature. The reaction was followed by TLC, and was complete in 2 hr. The brown mixture was poured into ice-water to deposit a yellow oil which was extracted into ether. The ethereal layer was washed with water, sat. $NaHCO_3$ aq and water, and dried (anhyd. Na_2SO_4). Concentration of the filtrate *in vacuo* gave pale yellow crystals, mp 46—91°, wt. 638 mg. They were chromatographed over 320 g silica gel (Kanto Chemical Co.). Elution with 300 ml 99: 1 benzene–ether gave XX as colorless needles, mp 123—124.5°, wt. 112 mg (18.0% yield). Recrystallization from MeOH gave sample of mp 126.5—127°. *Anal.* Calcd. for $C_{23}H_{34}O_4$: C, 73.76; H, 9.15. Found: C, 73.93; H, 9.24. $[\alpha]_D^{21}$ −147.5° (*c*=1.00). UV λ_{max} mμ(ε): 202 (6690) (>C_8=C_{14}<). IR ν_{max} cm^{-1}: 1738 (s) and 1730 (s) (2α- and 17β-$OCOCH_3$), 1657 (w) (C=C). NMR τ: 5.18 (1 proton, multiplet, half width =16 cps) (2β-H), 5.42 (1 proton, triplet, J=8 cps) (17α-H), 7.98 (3 protons, singlet) (17β-$OCOCH_3$), 8.01 (3 protons, singlet) (2α-$OCOCH_3$), 901 (3 protons, singlet) (18-H), 9.18 (3 protons, singlet) (19-H). Mass Spectrum *m/e*: 314 ($C_{21}H_{30}O_2$) (M^+-CH_3COOH).

Further elution with 1050 ml 99: 1 benzene–ether gave XXI as colorless needles, mp 113—116.5°, wt. 446 mg (71.7 % yield). Recrystallization from MeOH gave sample of mp 116—117°. *Anal.* Calcd. for $C_{23}H_{34}O_4$: C, 73.76; H, 9.15. Found: C, 73.76; H, 9.04. $[\alpha]_D^{22}$ −5.0° (*c*=1.01). UV λ_{max} mμ(ε): 209 (13230) (>C_9=C_{11}<$_H$). IR ν_{max} cm^{-1}: 3046 (m) ($_H$>C=C<), 1737 (s) and 1721 (s) (2α- and 17β-$OCOCH_3$), 1664 (w) and 1641 (w) (C=C). NMR τ: 4.60 (1 proton, multiplet) (11–H), 5.01 (1 proton, multiplet, half width=9 cps) (2β-H), 5.30 (1 proton, triplet, J=8 cps) (17α-H), 7.96 (3 protons, singlet) (17β-$OCOCH_3$), 8.03 (3 protons, singlet) (2α-$OCOCH_3$), 8.92 (3 protons, singlet) (19-H), 9.28 (3 protons, singlet) (18–H). Mass Spectrum *m/e*: 374 ($C_{23}H_{34}O_4$) (M^+).

Catalytic Hydrogenation of XXI: Formation of XVI——XXI (50 mg) was dissolved in 5.0 ml glacial acetic acid, and hydrogenated with 107 mg $PtO_2 \cdot H_2O$ as catalyst at 10°. After absorption of hydrogen ceased, the catalyst was filtered off, and the filtrate was concentrated *in vacuo* followed by addition of water to deposit colorless crystals. The crystals were extracted into ether, and the ethereal layer was washed with water, sat. $NaHCO_3$ aq and water, and dried (anhyd. Na_2SO_4). Concentration of the filtrate *in vacuo* gave colorless needles, mp 116—119°, wt. 48 mg. They were chromatographed over 25 g silica gel (Kanto Chemical Co.). Elution with 350 ml 99: 1 benzene–ether gave XVI as colorless needles, mp 121.5—123.5°, wt. 43 mg (85.5% yield). Recrystallization from MeOH gave sample of mp 125—125.5°, alone and on admixture with a sample of XVI. Their IR spectra were superposable. IR ν_{max} cm^{-1}: 1737 (s) and 1729 (s) (2α- and 17β-$OCOCH_3$).

Epoxidation of XXI with Perbenzoic Acid: Formation of 2α, 17β-Diacetoxy-9α,11α-epoxy-5β-androstane (XXII)——To a solution of XXI (433 mg, 1.16 mmoles) in 5.0 ml $CHCl_3$, 35.3 ml $CHCl_3$ solution of perbenzoic acid (containing 481 mg or 3.48 mmoles of the peracid) was added in the cold and the mixture kept at room temperature in dark; the reaction was complete in 25 hr (TLC). The amount of the peracid consumed was found to be 158 mg (0.99 equivalent to XXI) by titration of the remaining amount in the reaction mixture with 0.1N $Na_2S_2O_3$. The reaction mixture was washed with sat. Na_2SO_3 aq, water, sat. $NaHCO_3$ aq and water, and dried (anhyd. Na_2SO_4). Concentration of the filtrate *in vacuo* gave colorless needles of mp 127—132°, wt. 448 mg. They were chromatographed over 140 g silica gel (Kanto Chemical Co.). Elution with 1020 ml 32:1 benzene–ether gave XXII as colorless needles, mp 135.5—136.5°, wt. 418 mg (92.9% yield). Recrystallization from MeOH gave sample of mp 137.5—138.5°. *Anal.* Calcd. for $C_{23}H_{34}O_5$: C, 70.74; H, 8.78. Found:

C, 70.65; H, 8.82. $[\alpha]_D^{22}$ −84.0° (c=1.00). UV λ_{max} mμ (ε): end absorption at 210 (182). IR ν_{max} cm^{-1}: 1737 (s) and 1727 (s) (2α- and 17β-OCOCH$_3$), 930 (s) and 910 (s) (C–O–C). NMR τ: 5.23 (1 proton, multiplet, half width=14 cps) (2β-H), 5.46 (1 proton, triplet, J=8 cps) (17α-H), 7.13 (1 proton, doublet, J=5 cps) (11β-H), 7.99 (3 protons, singlet) 17β-OCOCH$_3$), 8.03 (3 protons, singlet) (2α-OCOCH$_3$), 8.85 (3 protons, singlet) (19–H), 9.23 (3 protons, singlet) (18-H). Mass Spectrum m/e: 390 ($C_{23}H_{34}O_5$) (M^+).

Reductive Ring Opening of XXII with Lithium–Ethylamine: Formation of 2α, 9α, 17β-Trihydroxy-5β-androstane (XXIII)——To a stirred solution of XXII (225 mg) in 23 ml ethylamine, 225 mg lithium was added in small pieces at 0°; the color of the reaction mixture turned to dark blue in 15 min and then to dark green in 105 min. The mixture was kept at room temperature until almost all ethylamine evaporated. Addition of water to the residue in the cold deposited colorless crystals, which were extracted into ether. The ethereal layer was washed with water, and dried (anhyd. Na_2SO_4). Concentration of the filtrate *in vacuo* gave colorless crystals of mp 239—255°, wt. 182 mg. They were chromatographed over 91 g silica gel (Kanto Chemical Co.). Elution with 780 ml 32: 1 ether–MeOH gave XXIII as colorless needles, mp 268—269.5°, wt. 142 mg (79.9% yield). Recrystallization from acetone gave sample of mp 270—271.5°. *Anal.* Calcd. for $C_{19}H_{32}O_3$: C, 73.98; H, 10.46. Found: C, 73.84; H, 10.68. $[\alpha]_D^{18}$ +77.3° (c=0.11). UV λ_{max}: transparent above 210 mμ. IR ν_{max} cm^{-1}: 3438 (s), 3338 (s), 3264 (s), 3196 (s) and 3116 (s) (2α-, 9α- and 17β-OH). Mass Spectrum m/e: 308 ($C_{19}H_{32}O_3$) (M^+), 290 ($C_{19}H_{30}O_2$) (M^+-H_2O), 272 ($C_{19}H_{28}O$) (M^+-2H_2O), 254 ($C_{19}H_{26}$) (M^+-3H_2O). This was insoluble to $CHCl_3$, and the measurement of NMR in $CDCl_3$ was not carried out.

Acetylation of XXIII: Formation of 2α,17β-Diacetoxy-9α-hydroxy-5β-androstane (XXIV)——To a solution of XXIII (50 mg) in 1.0 ml pyridine, 1.0 ml acetic anhydride was added dropwise in the cold, and the reaction mixture kept at room temperature. The reaction was followed by TLC, and was complete in 75 hr. The yellow reaction mixture was poured into ice–water to deposit colorless crystals, which were extracted into ether. The ethereal layer was washed with water, dil. H_2SO_4, water, sat. $NaHCO_3$ aq and water, and dried (anhyd. Na_2SO_4). Concentration of the filtrate *in vacuo* gave colorless needles of mp 91—102°, wt. 63 mg. They were chromatographed over 21 g silica gel (Kanto Chemical Co.). Elution with 240 ml 32: 1 benzene–ether gave XXIV as colorless needles, mp 102—104.5°, wt. 61 mg (96.1 % yield). Recrystallization from MeOH gave sample of mp 107—108.5°. *Anal.* Calcd. for $C_{23}H_{36}O_5$: C, 70.37; H, 9.24. Found: C, 70.38; H, 9.43. $[\alpha]_D^{26}$ −10.4° (c=1.01). UV λ_{max} mμ (ε): end absorption at 210 (160). IR ν_{max} cm^{-1}: 3531 (s) (OH), 1738 (s) and 1727 (s) (2α- and 17β-OCOCH$_3$). NMR τ: 4.90 (1 proton, multiplet, half width=8 cps) (2β-H), 5.31 (1 proton, triplet, J=8 cps) (17α-H), 6.66 (1 proton, singlet) (9α-OH), 7.93 (3 protons, singlet) (2α-OCOCH$_3$), 7.99 (3 protons, singlet) (17β-OCOCH$_3$), 8.93 (3 protons, singlet) (19-H), 9.23 (3protons, singlet) (18-H). Mass Spectrum m/e: 392 ($C_{23}H_{36}O_5$) (M^+), 332 ($C_{21}H_{32}O_3$) (M^+-CH_3COOH), 314 ($C_{21}H_{30}O_2$) (M^+-CH_3COOH-H_2O), 272 ($C_{19}H_{28}O$) (M^+-2CH_3COOH), 254 ($C_{19}H_{26}$) (M^+-2CH_3COOH-H_2O).

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