Structure–Reactivity Relationships in Normal and 19-Nor-5,10-seco-steroidal Cyclodecenone Systems. Part 1. Acid-catalyzed and Thermal Reactions[1]

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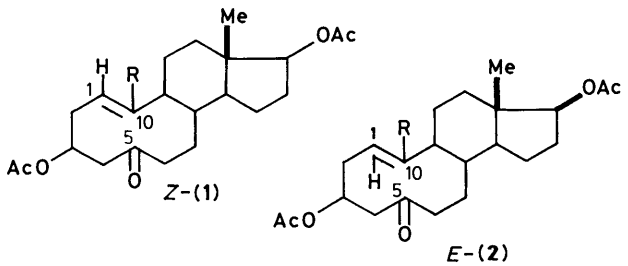
Under acid-catalyzed conditions both the (*Z*)- and (*E*)-19-nor-seco ketones (**1a**) and (**2a**) underwent transannular cyclization [forming the C(5)–C(10) bond], accompanied by aromatization of the resulting ring A, to give estra-1,3,5(10)-trien-17β-yl acetate (**4**) (in 76% and 83% yield, respectively). On the other hand, when the corresponding 19-methyl analogues (**1b**) and (**2b**) were treated with acid under similar experimental conditions, the (*Z*)-diastereoisomer (**1b**) remained mostly unchanged, while the (*E*)-19-methyl-seco ketone (**2b**) afforded the A-nor-B-homo derivative (**5**) (in 68% yield). The same transannular cyclization of the (*E*)-seco ketone (**2b**) was also achieved thermally in the absence of protonation.

As recently reported,[2] the mercuric oxide–iodine oxidation of 5-hydroxy-19-nor-5α-androstane-3β,17β-diyl diacetate results in the fragmentation of the C(5)–C(10) bond and formation of the two diastereomeric (*Z*)- and (*E*)-3β,17β-diacetoxy-19-nor-5,10-secoandrost-1(10)-en-5-ones (**1a**) and (**2a**), *i.e.* products containing a ten-membered ring (instead of the two fused steroid rings A and B), with an olefinic double bond bearing hydrogen atoms at both C(1) and C(10).

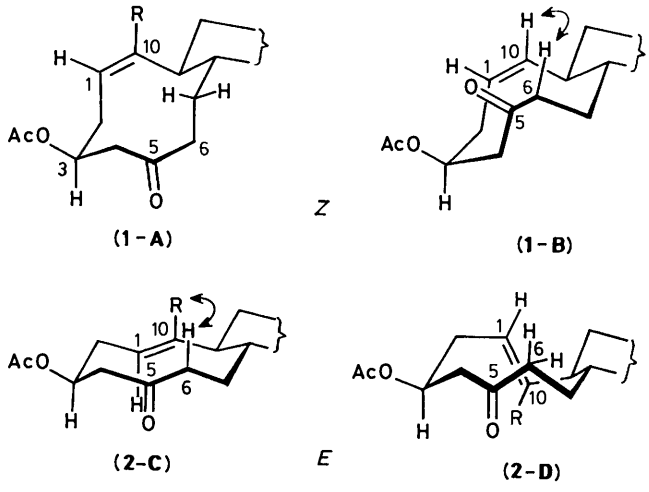


a; R=H
b; R=Me

Our previous investigations have shown the following. (i) That the structurally analogous (*Z*)- and (*E*)-5,10-seco ketones of the 'normal' (*i.e.* 19-methyl containing) steroid (actually cholestane) series [(**1b**) and (**2b**), but with cholestane side-chain] behave differently towards reagents which can effect,[3,4] or participate[5] in, reactions involving bond formation across the ten-membered ring. This is due to different stereochemical characteristics of the (*Z*)- and (*E*)-cyclodecenone system,[6,7] the (*E*)-seco ketone [of type (**2b**)] being far more reactive in these transannular processes than the (*Z*)-diastereoisomer [of type (**1b**)].

(ii) That the conformations of the ten-membered ring in both the (*Z*)- and (*E*)-19-nor-5,10-seco steroid compounds closely resemble the respective conformations in the corresponding 19-methyl containing analogues (Figure **1-A** and **2-C**, respectively).[2]

Therefore, it was considered of interest to examine the possible transannular reactions in the 19-nor-5,10-seco steroid series too. In the present study, the transannular reactivity of the (*Z*)- and (*E*)-3β,17β-diacetoxy-19-nor-5,10-secoandrost-1(10)-en-5-ones, (**1a**) and (**2a**), under acid-catalyzed and thermal conditions, has been investigated and compared with the reactivity of the corresponding 19-methyl containing derivatives (**1b**) and (**2b**), when subjected to similar reaction conditions.

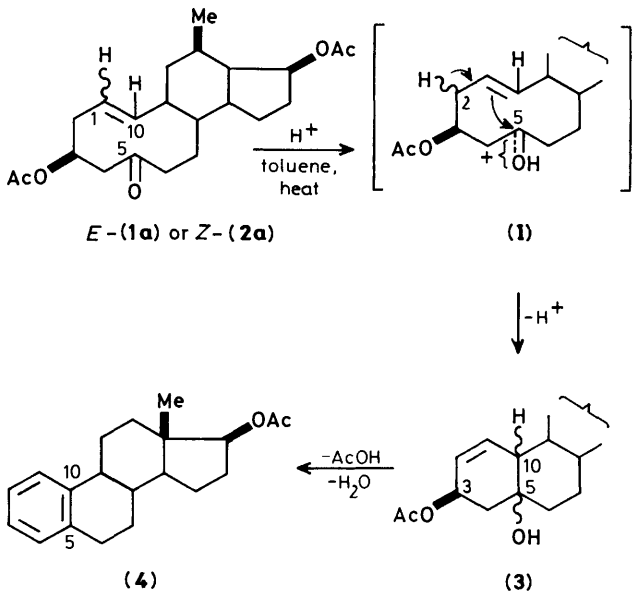


a; R=H
b; R=Me

Figure. Conformations of the ten-membered ring (in solution) in the steroidal (*Z*)- and (*E*)-5,10-seco 5-ketones (**1a**), (**1b**), (**2a**), and (**2b**). Ground state (and similar transition state) conformations (**1-A**) and (**2-C**); other possible reactive (transition state) conformations (**1-B**) and (**2-D**).

The acid-catalyzed reactions were performed in boiling toluene in the presence of toluene-*p*-sulphonic acid as the proton donor. It was found that, under these conditions, both the (*Z*)- and (*E*)-19-nor-seco ketones, (**1a**) and (**2a**) respectively, underwent cyclization (Scheme 1), by way of transannular C(5)–C(10) bond formation, accompanied by aromatization of the resulting ring A. This is accomplished by thermal elimination of water and acetic acid from the originally formed cyclic intermediate(s) [of type (**3**)], to give, after 48 h as practically the only reaction product, estra-1,3,5(10)-trien-17β-yl acetate† (**4**) (in 76 and 83% yield, respectively).‡ A by-product, isolated in this reaction in low yield (2—5%) from the (*E*)-nor-seco ketone (**2a**), according to its i.r. and ^{1}H n.m.r. spectral data, is believed

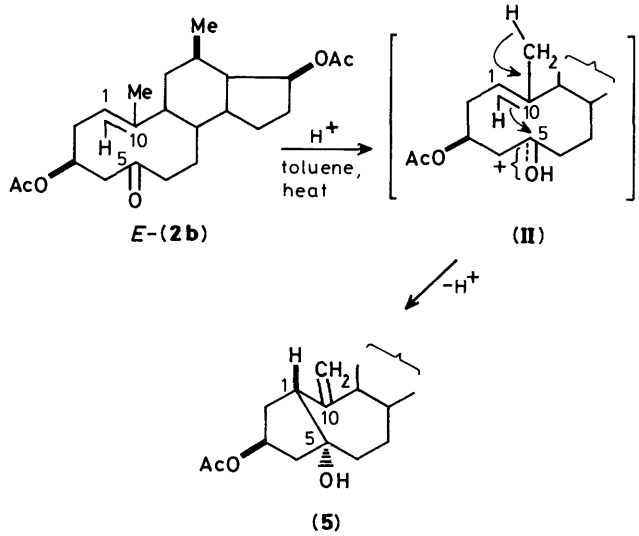
† This aromatic steroid (**4**) was obtained previously by other routes.[8]
‡ Since *ca.* 22 and 12% of the respective (*Z*)- and (*E*)-nor-seco ketones (**1a**) and (**2a**) were recovered in these reactions, the yield of cyclization, based on reacted substrate, amounted in both cases to over 95%.



Scheme 1.

to have structure (**3**), particularly since it underwent fast aromatization to (**4**) when treated with toluene-*p*-sulphonic acid in boiling toluene (as above). However, its stereochemistry at C(5) and C(10) is not known.

On the other hand, when a similar acid-catalyzed reaction was applied to the 19-methyl containing analogues, (**1b**) and (**2b**), the (*Z*)-5,10-seco ketone (**1b**) remained mostly unchanged (> 95%) (the part which reacted consisted of an unresolvable mixture). The corresponding *E*-diastereoisomer (**2b**), as expected from previous studies of similar systems,[3,9] readily underwent transannular cyclization (Scheme 2), to produce,



Scheme 2. The *Z*-isomer (**1b**) did not react

after 6 h under reflux, 5-hydroxy-5(10 ⟶ 1βH)*abeo*-5α-androst-10(19)-ene-3β,17β-diyl 3,17-diacetate (**5**), in *ca.* 68% yield [*i.e.* 87%, based on reacted substrate (**2b**)].

The structure of product (**5**) was deduced on the basis of elemental microanalyses ($C_{23}H_{34}O_5$) and spectral results (^{1}H n.m.r. and i.r.). These revealed the presence of an exocyclic methylene double bond (two singlets at δ 4.97 and 5.08 in the n.m.r. spectrum, and i.r. absorption at 3 080 and 1 620 cm^{-1}), and an intramolecularly hydrogen bonded OH group (a sharp i.r. band at 3 540 cm^{-1} observed in CCl_4 solution, regardless of the used molar concentration). Moreover, appearance of this i.r. absorption was taken as evidence of the *trans*-1β,5α-stereochemistry at the bridging sites of the nor-A and homo-B rings in product (**5**).* Further structural proof for (**5**) was obtained by comparison of spectral data with those of analogous products discussed previously.[3,4]

It should be noted that the 19-methyl containing (*E*)-seco ketone (**2b**) underwent acid-catalyzed cyclization also at lower temperature, *i.e.* at 80 °C in benzene, to give (after heating for 24 h) product (**5**) in 48% yield (73%, based on consumed starting material). In contrast, in the 19-nor series neither the (*Z*)- nor the (*E*)-seco ketone, (**1a**) and (**2a**), reacted under these conditions, even after 48 h in refluxing benzene.

In order to examine the thermal reactivity of the steroidal 5,10-seco-1(10)-en-5-one systems, each of the four substrates (**1a**), (**2a**), (**1b**), and (**2b**) was heated in boiling toluene solution for 48 h, in the absence of a proton donor. It was found that, under these conditions, only the 19-methyl containing (*E*)-seco ketone (**2b**) underwent cyclization, to give the previously obtained product (**5**), in 47% yield (48% of starting material being recovered).† Similar thermolysis of the other three substrates (**1b**), (**1a**), and (**2a**) gave only the unchanged starting seco ketones.

From these findings it follows that the transannular reactivity (in the presence of acid or only upon heating) of the (*Z*)- and (*E*)-cyclodecenone systems, incorporated in the modified 5,10-seco steroids of type (**1**) and (**2**), is highly influenced by the presence or absence of the 19-methyl group. Thus, inspection of molecular models reveals that in the (*Z*)-seco ketone series (**1**), in order to undergo transannular reaction, the molecules of (**1a**) and (**1b**) must, in the transition state, change their ground-state conformation (**1-A**) to the less stable form (**1-B**) (Figure).‡ Since the 19-nor (*Z*)-compound (**1a**) undergoes transannular cyclization (Scheme 1) when treated with acid (forming the C(5)–C(10) bond), and the 19-methyl containing (*Z*)-analogue (**1b**) does not, it seems reasonable to assume that the inability of the latter seco ketone (**1b**) to cyclize under these conditions, may be explained by the steric repulsion between the 19-methyl group and the transannular 6β-hydrogen atom in conformation (**1b-B**). This would prevent the reaction centres [*i.e.* the 5-keto carbonyl group and the olefinic 1(10)-double bond] from approaching close enough for bonding interaction.

A similar unfavourable repulsion between the 19-methyl group and the 6β-hydrogen exists also in the transition state conformation corresponding to the ground-state conformation (**2b-C**) of the 19-methyl containing (*E*)-seco ketone (**2b**) (Figure). Therefore, this compound (**2b**) reacts in the less populated conformation (**2b-D**). However, for cyclization this is the more favourable and reactive transition state, and leads to the formation of the transannular C(1)–C(5) bond affording the A-nor-B-homo steroid product (**5**) with the 1β,5α-configuration (Scheme 2).§ However, on the basis of present data [formation

* This intramolecular hydrogen bond in (**5**) is formed between the 5-hydroxy group and the π-electrons of the exocyclic methylene 10(19)-double bond. As shown for similar systems in the cholestane series, this interaction is only possible (for steric reasons) when the cyclization products [of type (**5**)] have the 1β,5α-configuration.[4,9]

† This result suggests that part of the cyclization product (**5**), obtained in the above described acid-catalyzed reaction of (**2b**), could have arisen also from the thermal transformation.

‡ In conformation (**1-A**), because of a too great distance between the 1(10)-double bond and the 5-keto carbonyl group, transannular 5,10- or 1,5-ring closure is not possible.[3,7]

§ A similar situation was also observed in the cholestane series.[4,6]

of (**4**)] (Scheme 1), it is not possible to specify which conformation [(**2a**-**C**) or (**2a**-**D**), Figure] is involved in the transannular cyclization of the (*E*)-19-nor-seco ketone (**2a**), since in this case both conformations (**C**) and (**D**) in the transition state can undergo bond formation across the ten-membered ring.

In addition, the presence or absence of the 19-methyl group in the starting seco ketone determines the regiospecificity of the transannular reactions, whereby the 19-methyl containing (*E*)-seco ketone (**2b**) affords the A-nor-B-homo derivative (**5**), this being due to the more favourable potential tertiary C(10) carbo-cationic site in the transition state structure (**II**) (Scheme 2). On the other hand, the (*Z*)- and (*E*)-19-nor compounds, (**1a**) and (**2a**), respectively, through transition states of type (**I**) (Scheme 1), give the 'natural' steroid system with the two fused six-membered rings A and B, the stability of which is enhanced by aromatization of ring A (**4**).

Experimental *

All m.p.s are uncorrected. Optical rotations were measured in $CHCl_3$ solution (if not stated otherwise). ^1H N.m.r. spectra were obtained at 100 MHz with a Varian HA spectrometer in deuteriochloroform with tetramethylsilane as internal reference (chemical shifts are reported in p.p.m. as δ values). I.r. spectra were determined on a Perkin-Elmer double-beam instrument, model 337. Silica gel (0.05—0.2 mm) was used for preparative column chromatography. Control of the reactions and separation of products were monitored by t.l.c., which was carried out on silica gel G (Stahl) with benzene–ethyl acetate (9:1 or 7:3), detection being effected with 50% aqueous sulphuric acid. Light petroleum refers to the fraction b.p. 40—60 °C.

(*Z*)-3β,17β-Diacetoxy-19-nor-5,10-secoandrost-1(10)-en-5-one (**1a**)[2] had m.p. 159—160 °C (from acetone–light petroleum); $[\alpha]_D^{20}$ +99.2° (*c* 1.03); $\nu_{max.}$(KBr) 1 750, 1 740, 1 705, 1 250, 1 235, and 1 020 cm^{-1} (Found: C, 70.45; H, 8.5. Calc. for $C_{22}H_{32}O_5$: C, 70.18; H, 8.57%). (*E*)-3β,17β-Diacetoxy-19-nor-5,10-secoandrost-1(10)-en-5-one (**2a**)[2] had m.p. 208—209 °C (from acetone–light petroleum); $[\alpha]_D^{20}$ +51.8° (*c* 1.05); $\lambda_{max.}$(MeOH) 212 nm (ε 2 800);† $\nu_{max.}$(KBr) 1 740, 1 730, 1 705, 1 245, 1 235, and 1 022 cm^{-1} (Found: C, 70.2; H, 8.5. Calc. for $C_{22}H_{32}O_5$: C, 70.18; H, 8.57%).

Preparation of (Z)-3β,17β-*Diacetoxy*-5,10-*secoandrost*-1(10)-*en*-5-*one* (**1b**).—A mixture of 5-hydroxy-5α-androstane-3β,17β-diyl 3,17-diacetate (1.96 g),[12] lead tetra-acetate (10.35 g), and iodine (2.16 g), in cyclohexane (200 ml), was stirred and irradiated for 3 h without heating with a 500-W tungsten lamp placed in a central water- and air-cooled jacket. The precipitate was filtered off and the filtrate washed successively with water, aqueous 10% sodium thiosulphate, aqueous sodium hydrogen carbonate, and water, dried ($MgSO_4$), and evaporated under reduced pressure. The residue (*ca.* 2.5 g) was chromatographed on silica gel (100 g). Elution with benzene and benzene–ether (9:1) gave a complex mixture (162 mg) which was not investigated. Elution with benzene–ether (9:1) afforded a crystalline solid (1.12 g), which was twice recrystallized from methanol to give (*Z*)-3β,17β-diacetoxy-5,10-secoandrost-1(10)-en-5-one (**1b**) (791 mg, 41%), m.p. 156 °C; $[\alpha]_D^{20}$ +45° (*c* 0.20, dioxane); $\nu_{max.}$(KBr) 1 735, 1 700, 1 240, and 1 030 cm^{-1}; δ 0.81 (3 H, s, 18-H), 1.69 (3 H, d, 19-H), 2.02 (6 H, two s, 3-OAc and 17-OAc), 2.37 (1 H, m, 4-H_e), 3.26 (1 H, m, 4-H_a), 4.67 (1 H, t, 17-H), and 5.15—5.45 (2 H, br m, 1-H and 3-H) (Found: C, 70.65; H, 8.8. $C_{23}H_{34}O_5$ requires C, 70.74; H, 8.78%).

Preparation of (E)-3β,17β-*Diacetoxy*-5,10-*secoandrost*-1(10)-*en*-5-*one* (**2b**).—Lead tetra-acetate (7.0 g) and dry $CaCO_3$ (1.5 g) were added to a solution of 5-hydroxy-5α-androstane-3β,17β-diyl diacetate (1.96 g) in anhydrous benzene (220 ml), placed in a quartz cylindrical irradiation vessel. The vigorously stirred mixture was irradiated at room temperature with a high pressure Hg-lamp (TQ 150 Z2, Hanau), contained in a central, water-cooled jacket. After 1.5 h the iodine-starch test for Pb^{IV} was negative. The precipitate was filtered off, and the filtrate was washed successively with water, aqueous sodium hydrogen carbonate, and water, dried ($MgSO_4$), and evaporated under reduced pressure. The crude oxidation mixture was chromatographed on silica gel (100 g). Elution with benzene gave a complex mixture (214 mg). Benzene–ether (9:1) eluted a crystalline mixture mainly of (*Z*)- and (*E*)-stereoisomer (900 mg, 46%), which was twice recrystallized from acetone–methanol to give (*E*)-3β,17β-diacetoxy-5,10-secoandrost-1(10)-en-5-one (**2b**) (434 mg, 22%), m.p. 130—132 °C; $[\alpha]_D^{20}$ +10° (*c* 0.20, dioxane); $\lambda_{max.}$(EtOH) 225 nm (ε 2 360); $\nu_{max.}$(KBr) 1 730, 1 700, 1 245, and 1 030 cm^{-1}; δ 0.82 (3 H, s, 18-H), 1.76 (3 H, s, 19-H), 2.02 (6 H, two s, 3-OAc and 17-OAc), 4.60 (1 H, t, 17-H), 4.84 (1 H, m, 1-H), and 5.35 (1 H, m, 3-H) (Found: C, 70.7; H, 8.75. $C_{23}H_{34}O_5$ requires C, 70.74; H, 8.78%).

Acid-catalyzed Cyclization of (Z)-3β,17β-*Diacetoxy*-19-*nor*-5,10-*secoandrost*-1(10)-*en*-5-*one* (**1a**).—Toluene-*p*-sulphonic acid (20 mg) was added to the (*Z*)-19-nor-seco ketone (**1a**) (200 mg) in dry toluene (100ml), and the resulting solution was heated under reflux for 48 h. It was diluted with ether, washed with aqueous sodium hydrogen carbonate and water, dried ($MgSO_4$), and evaporated under reduced pressure. The resulting mixture was chromatographed on silica gel (8 g). Elution with benzene–light petroleum (1:1) afforded estra-1,3,5(10)-trien-17β-yl acetate (**4**) (121 mg, 76%), m.p. 119—120 °C (from acetone–light petroleum) (lit.,[8] 119—121 °C); $[\alpha]_D^{20}$ +42° (*c* 1.0) (lit.,[8] $[\alpha]_D^{20}$ +46°); $\nu_{max.}$(KBr) 1 740, 1 245, and 745 cm^{-1}; δ 0.80 (3 H, s, 18-H), 1.98 (3 H s, 17-OAc), 4.60 (1 H, t, 17-H), and 7.00 (4 H, m, ArH) (Found: C, 80.7; H, 8.6. $C_{20}H_{26}O_2$ requires C, 80.50; H, 8.78%). Benzene–ether (94:6) eluted unchanged starting material (**1a**) (44 mg, 22%), m.p. 159—160 °C (undepressed by admixture with an authentic sample).

Acid-catalyzed Cyclization of (E)-3β,17β-*Diacetoxy*-19-*nor*-5,10-*secoandrost*-1(10)-*en*-5-*one* (**2a**).—A solution of the (*E*)-19-nor-5,10-seco ketone (**2a**) (200 mg) and toluene-*p*-sulphonic acid (20 mg) in dry toluene (100 ml) was heated under reflux for 48 h. The mixture was worked up as described above and chromatographed on silica gel (8 g). Elution with benzene–light petroleum (1:1) gave estra-1,3,5(10)-trien-17β-yl acetate (**4**) (132 mg, 83%), m.p. 120—121 °C (from acetone–light petroleum). Benzene–ether (96:4) eluted unchanged starting material (**2a**) (24 mg, 12%), m.p. 208 °C (undepressed by admixture with an authentic sample). Elution with benzene–ether (9:1) afforded product (**3**) (8 mg, 4%); $\nu_{max.}$(CCl_4) 3 520, 1 745, 1 245, and 1 030 cm^{-1}; δ 0.83 (3 H, s, 18-H), 2.04 (6 H, two s, 3-OAc and 17-OAc), 4.60 (1 H, t, 17-H), and 5.15—5.30 (3 H, br m, 1-H, 2-H, 3-H). A solution of compound (**3**) (6 mg) and toluene-*p*-sulphonic acid (2 mg) in toluene (10 ml) was refluxed for 1 h. Work-up gave quantitatively (as monitored by t.l.c.) estra-1,3,5(10)-trien-17β-yl acetate (**4**) [i.r. spectrum identical with that of authentic (**4**)].

* We thank Dr. R. Tasovac (Microanalytical Laboratory, Faculty of Science, Belgrade) for carrying out elemental microanalyses. I.r. and n.m.r. spectra were recorded in the Laboratories for Instrumental Analyses, Faculty of Science, Belgrade (direction Prof. D. Jeremić).

† Only the (*E*)-seco ketones [of type (**2**), and not the (*Z*)-isomers (**1**)] show a short wavelength u.v. absorption,[2,9,10] arising from photodesmotic transition[11] {*i.e.* spatial proximity of the 1(10)-double bond and 5-keto carbonyl group [as in (**1**-**C**), Figure 1]}.

Acid-catalyzed Cyclization of (E)-3β,17β-*Diacetoxy*-5,10-*secoandrost*-1(10)-*en*-5-*one* (**2b**).—A solution of the (*E*)-5,10-seco ketone (**2b**) (200 mg) and toluene-*p*-sulphonic acid (20 mg) in toluene (100 ml) was heated under reflux for 6 h. The mixture was worked up as above and chromatographed on silica gel (8 g). Benzene–ether (95:5) eluted unchanged starting material (**2b**) (45 mg, 22%), m.p. 130—132 °C (undepressed upon admixture with an authentic sample). Elution with benzene–ether (9:1) gave 5-hydroxy-5(10 ⟶ 1βH)*abeo*-5α-androst-10(19)-ene-3β,17β-diyl diacetate (**5**) (136 mg, 68%), m.p. 96—98 °C (from acetone–light petroleum); $[\alpha]_D^{20}$ +13.6° (*c* 0.90); $\nu_{max.}$(KBr) 3 520, 3 500, 3 080, 1 730, 1 720, 1 620, 1 235, 1 200, 1 040, and 1 014 cm^{-1}; $\nu_{max.}(CCl_4)$ 3 540, 3 080, 1 730, 1 620, 1 240, 1 045, and 1 020 cm^{-1}; δ 0.82 (3 H, s, 18-H), 1.95 (6 H, two s, 3-OAc and 17-OAc), 2.25 (1 H, m, 2-H), 2.48 (1 H, m, 4-H), 2.88 (1 H, m, 1-H), 4.55 (1 H, t, 17-H), 4.97 and 5.08 (2 H, two s, 19-H), *ca.* 5.10 (1 H, br m, 3-H) (Found: C, 70.6; H, 8.9. $C_{23}H_{34}O_5$ requires C, 70.74; H, 8.78%).

Thermal Cyclization of (E)-3β,17β-*Diacetoxy*-5,10-*seco-androst*-1(10)-*en*-5-*one* (**2b**).—A solution of the (*E*)-5,10-seco ketone (**2b**) in toluene (100 ml) was refluxed for 48 h and then evaporated under reduced pressure. The resulting mixture was chromatographed on silica gel (8 g), giving [by elution with benzene–ether (95:5)] 96 mg (48%) of starting material (**2b**) (m.p. undepressed by admixture with an authentic sample) and [by elution with benzene–ether (90:10)] the cyclization product (**5**) (94 mg, 47%) which was identified on the basis of a m.p. and mixed m.p. determination and by i.r. and ^1H n.m.r. spectral results.

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