18 hr gave an amorphous mixture displaying the ultraviolet maximum of the 4,8-dihydroxydiene **15**, 295 nm (9900); isolation of the pure compound failed.

4,17-Dioxo-3,4-secoandrosta-5,7-dien-3-oic Acid (12). A. From the Epidioxide 7a.—The epidioxide **7a** (0.85 g) in 10 ml of acetic acid was heated at 95° for 1.5 hr and the solvent was distilled. The crystalline residue resulting after ether trituration was washed with cold ethyl acetate and recrystallized from methylene chloride–ethyl acetate to yield 0.15 g of the seco acid **12**: mp 169–170°; 3.0–3.2 (shoulder), 5.72, 5.81, 5.92 μ; 320 nm (13,600); no change in the uv maximum was seen in the presence of either acid or base; 47 (18-CH_3), 74 (19-CH_3), 361 (d, J = 9 Hz, C=CH), 405 Hz (d, J = 9 Hz, C=CH).

Anal. Calcd for $C_{19}H_{24}O_4$: C, 72.12; H, 7.65. Found: C, 72.11; H, 7.55.

The same reaction required 5 days at room temperature to go to completion. Uv analysis of the total product in either case implied *ca.* 50% was the seco acid **12**.

B. From the Oxide 8.—A solution of 0.10 g of the oxide **8** in 5 ml of acetic acid was allowed to stand at room temperature for 2 hr and was then diluted with water. Methylene chloride extraction afforded 60 mg of crude product [λ_{max} 316 mμ (6600)] having the characteristic nmr and ir absorption spectra of the seco acid **12**. When the reaction was run in deuterioacetic acid and followed directly in an nmr cell, the reaction required a longer period of time for completion (*ca.* 18 hr); no intermediate was visible and no other discernible product was formed.

Treatment of 75 mg of pure **12** in tetrahydrofuran with an excess of ethereal diazomethane afforded an amorphous methyl ester: 3.64, 5.72, 5.93 μ; 318 nm (11,550). The major nmr signals were the same as those of the acid **12** with the addition of the 218-Hz signal (OCH_3). Treatment of this ester (or the oxide **8**) with methanolic acid gave a complex acetal mixture lacking the diene chromophore.

Hydrogenation of the seco acid **12** in ethanol with a palladium/charcoal catalyst effected uptake of 2 mol equiv of hydrogen. The product was an amorphous aldehydro acid lacking uv absorption.

Registry No.—**1c**, 23971-00-8; **1c** 3-acetate, 29851-14-7; **2a**, 23970-97-0; **2a** acetate, 23970-96-9; **2b**, 23970-98-1; **2b** diacetate, 29851-17-0; **2c**, 23971-02-0; **2c** 3-acetate, 29851-19-2; **3a**, 29851-20-5; **3a** 3-acetate, 29851-21-6; **4a**, 23970-99-2; **4b**, 23971-01-9; **4c**, 29851-24-9; **5a**, 29851-25-0; **5a** diacetate, 29851-26-1; **6a**, 29851-41-0; **6a** acetate, 29851-40-9; **6c**, 29851-27-2; **7a**, 29851-28-3; **7c**, 29851-29-4; **8**, 29851-30-7; **9a**, 29851-31-8; **9a** 3-acetate, 29851-32-9; **9a** diacetate, 29851-33-0; **10**, 29851-34-1; **11**, 29851-35-2; **12**, 29936-63-8; **13a**, 29851-36-3; **13c**, 29851-37-4.

Acknowledgment.—The competent technical assistance rendered by Mrs. Barbara Tucker is gratefully acknowledged by the author.

Steroidal Adducts. IV.[1] Variable Selectivity in Hydride Reductions of a Steroidal Cyclic Anhydride

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Variable selectivity has been observed in different hydride reductions of a steroidal cyclic anhydride to γ-lactones. There is strong selectivity with lithium aluminum hydride, less with sodium aluminum hydride, and none with sodium borohydride. Lactol formation *via* reduction of the anhydride with lithium aluminum tri-*tert*-butoxyhydride is also highly selective. These results support a proposed mechanism involving 1,4 attack by hydride on a complex involving an anhydride group, another carbonyl group, and a metal cation.

Steroids bearing appropriate functional groups are unsurpassed in their ability to reveal the stereochemical aspects of a wide variety of important reactions. In a previous paper in this series,[3] a study was made of the reduction of cyclic anhydrides by metal hydrides to γ-lactones, a reaction of considerable potential synthetic utility. In particular, the Inhoffen adduct **1**[4,5] of ergosteryl acetate and maleic anhydride was shown to be reduced selectively by sodium borohydride or lithium aluminum hydride to the lactone **2**. None of the isomeric **3** was obtained. Bloomfield and Lee[6] proposed for reductions of simple succinic anhydrides that differences in the steric environment of anhydride carbonyl groups induce preferential participation of these carbonyls in an intermolecular complex also involving a reagent cation. The complex is then selectively attacked by the hydride reagent. The 3′- and 4′-carbonyls of **1** are approximately equivalent in steric environment[3] (C-3′ is only slightly more hindered), and hence the high degree of selectivity observed in the reduction of **1** to **2** could not be ascribed to intermolecular complex formation alone. It can, however, be interpreted[3] in terms of a mechanism in which intramolecular complex **4** is formed, and the bulky solvated **4** is then attacked by hydride at the other anhydride carbonyl. This mechanism was also invoked[3] to explain the selective reduction of **1** by lithium aluminum tri-*tert*-butoxyhydride to the lactol **5**. (A related reduction in the aromatic series, of a dimethoxyphthalic anhydride to a hydroxyphthalide, has also been reported.)[7]

To test the validity of this mechanism, we have investigated the hydride reduction of the methoxy anhydride **6**. This compound, lacking the acetoxycarbonyl group to participate in an intramolecular complex, might be expected to give both possible lactones **7** and **8** on hydride reductions provided that intermolecular complex formation is absent or itself unselective.

The methoxy anhydride **6** was prepared from the Inhoffen adduct **1**. The known hydroxydicarboxylic diester **9**[5,8] with diazomethane and aluminum chloride[9]

(1) For part III, see A. L. Andrews, R. C. Fort, and P. W. Le Quesne, *J. Org. Chem.*, **36**, 83 (1971).

(2) To whom inquiries should be addressed.

(3) M. E. Birckelbaw, P. W. Le Quesne, and C. K. Wocholski, *J. Org. Chem.*, **35**, 558 (1970).

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(5) D. N. Jones, P. F. Greenhalgh, and I. Thomas, *Tetrahedron*, **24**, 297 (1968).

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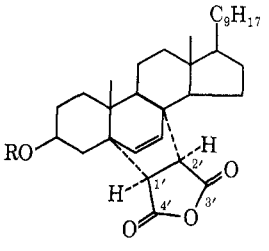
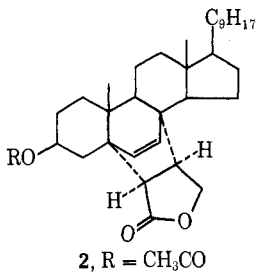
(7) D. Taub, N. N. Girotra, R. D. Hoffsommer, C. H. Kuo, H. L. Slates, S. Weber, and N. L. Wendler, *Tetrahedron*, **24**, 2443 (1968).

(8) D. N. Jones and I. Thomas, *J. Chem. Soc.*, 5206 (1964).

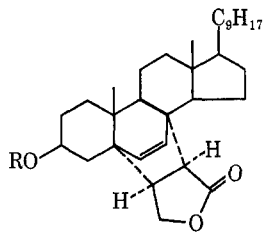
(9) E. Müller, R. Heischkeil, and M. Bauer, *Justus Liebigs Ann. Chem.*, **677**, 55 (1964).



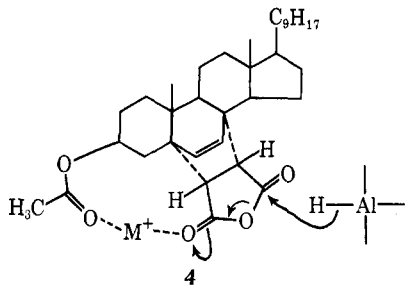
1, R = CH_3CO
6, R = CH_3



2, R = CH_3CO
7, R = CH_3
12, R = H



3, R = CH_3CO
8, R = CH_3



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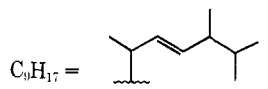
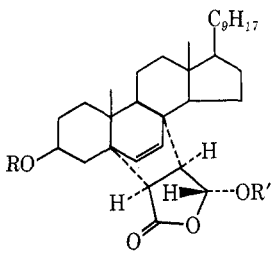
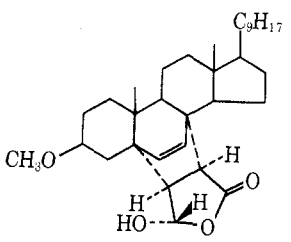


gave the methoxy dimethyl ester **10**, $C_{35}H_{54}O_5$, mp 92–93°, which on hydrolysis with potassium hydroxide in aqueous propylene glycol followed by reflux with acetic



5, R = CH_3CO; R′ = H
13, R = CH_3O; R′ = H
15, R = CH_3O; R′ = CH_3CO



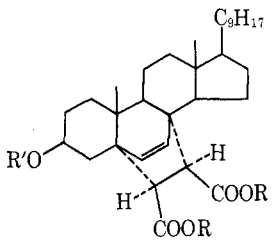
14

anhydride gave the desired methoxy anhydride **6**, $C_{33}H_{48}O_4$, mp 168–169.5°. That this compound has the same stereochemistry as the Inhoffen adduct **1** was established by comparison of their nmr spectra which are very closely analogous (see Table I).[10]

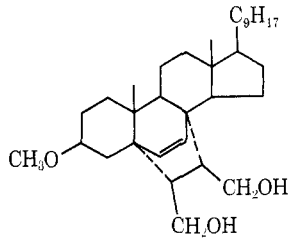
By treatment of the methoxy anhydride **6** with sodium borohydride in refluxing dioxane,[3] and chromatography of the crude product on alumina, a lactonic fraction was obtained which was shown by tlc to contain two compounds. These were separated by preparative tlc on silica gel and shown to be isomeric methoxy lactones, $C_{33}H_{50}O_3$. These compounds, mp 161–163° (slower moving on tlc) and mp 168–170.5° (faster moving in tlc), were obtained in virtually equal amounts and were assigned structures **7** and **8**, respectively, from the following data. First, both compounds with lithium aluminum hydride in refluxing dioxane gave the same methoxydiol **11**, $C_{33}H_{54}O_3$, mp

TABLE I
NMR SPECTRA OF ANHYDRIDES 1 AND 6 (τ UNITS)

Protons attached to	Anhydride 1	Anhydride 6
C-6, C-7 H	AB q, 3.86, 4.28 ($J_{6,7}$ = 8 Hz)	AB q, 3.83, 4.49 ($J_{6,7}$ = 8 Hz)
C-22, C-23 H	m, 4.90	m, 4.87
C-1′, C-2′ H	AB q, 6.58, 7.18 ($J_{1',2'}$ = 9 Hz)	AB q, 6.58, 7.17 ($J_{1',2'}$ = 9 Hz)
CH_3COO	s, 8.00	
CH_3O		s, 6.58
C-18 CH_3	s, 9.28	s, 9.28
C-19 CH_3	s, 8.98	s, 8.96



9, R = CH_3; R′ = H
10, R = R′ = CH_3



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190.5–191.5°. Secondly, treatment of the hydroxy lactone **12** of known structure[3] with diazomethane–aluminum chloride gave the slower moving methoxy lactone unambiguously. In accord with this, the ORD curve of the methoxy lactone **7**, was virtually superimposable on that of the acetoxy lactone **2** (see Experimental Section). The CD of **7** was also negative, as predicted from the lactone sector rules.[11] In contrast, the CD curve of the isomeric lactone **8** was positive, also in accord with predictions from the lactone sector rules. The ORD curve of this compound, however, has a positive peak (230 nm) followed by a negative trough (208 nm). This complexity may be regarded as an effect of the combined asymmetry of the whole molecule.[12] Thirdly, the nmr spectra of the two lactones, although similar, showed differences in accord with the structures assigned. The salient features are shown in Table II.

With lithium aluminum hydride in tetrahydrofuran at −55°, the methoxy anhydride **6** gave both lactones **7** and **8**, but under these conditions the lactone **7** greatly predominated (~13:1). Sodium aluminum hydride under the same conditions also gave both lactones, with slightly but reproducibly lesser selectivity (10:1).

These products were obtained in moderate (30–60%) yield. Other products were mixtures and were not

(10) Note that in ref 3 the J values quoted are *half* the values intended; this error does not, however, invalidate the structural conclusions drawn.

(11) J. P. Jennings, W. Klyne, and P. M. Scopes, *J. Chem. Soc.*, 7211, 7229 (1965).

(12) Compare C. Djerassi, in "Optical Rotatory Dispersion and Circular Dichroism in Organic Chemistry," Sadtler Research Laboratories, Philadelphia, Pa., 1967, p 16.

TABLE II
NMR SPECTRA OF LACTONES 7 AND 8

Protons attached to	Lactone 7	Lactone 8
C-6, C-7	AB q, 3.86, 4.32 (J_{AB} = 8 Hz)	AB q, 3.94, 4.24 (J_{AB} = 8 Hz)
C-22, C-23	m, 4.88	m, 4.89
C-3′ (2 H)	m, 6.1	
C-4′ (2 H)		m, ~6.1
C-1′	d, 7.64 (J = 9 Hz)	m, ~6.3
CH_3O	s, 6.72	s, 6.63
C-2′	m, 6.24	d, 7.08 (J = 10 Hz)
C-18	s, 9.28	s, 9.24
C-19	s, 8.97	s, 8.98

well characterized, but preliminary examination suggested the presence of acidic compounds.

Dreiding models of anhydride **6** do not indicate a large difference in the steric accessibility of the two carbonyl groups (the C-3′ group is slightly more hindered). The pronounced selectivity observed with lithium aluminum hydride at −55° probably, therefore, reflects a preferential complex formation involving the slightly less hindered C-4′ carbonyl, a lithium cation, and a carbonyl group from another molecule. The small lithium cation would be highly solvated, adding to the effective steric bulk of such a complex and enhancing the selectivity of its formation. The lesser selectivity of sodium aluminum hydride reduction may reflect lesser solvation of the metal cation in the complex. In the sodium borohydride reaction, the sodium cation, the much higher temperature, and perhaps the different solvent (dioxane) would tend to lessen the selectivity of intermolecular complex formation.

These data taken together support the formation of intermolecular complexes containing metal cations in the reduction of the methoxy anhydride **6**, as suggested for simpler compounds in Bloomfield and Lee's hypothesis,[6] and are also clearly consonant with the intramolecular complex formation proposed for the Inhoffen adduct **1**.[3]

Treatment of the anhydride **6** with lithium aluminum tri-*tert*-butoxyhydride gave mainly one compound, $C_{33}H_{50}O_4$, mp 234–237° dec. This compound is assigned the lactol structure **13** from comparison of its spectra (and those of its acetate **15**, $C_{35}H_{52}O_5$, mp 170–172°) with those of the acetoxy lactol **5** and from its reduction by sodium borohydride in ethanol to the lactone **7**. The ir spectrum of the lactol **13** in the solid state indicated the presence of both lactol and aldehydo acid tautomers but in chloroform solution only the ring-closed form. The stereochemistry of the lactol OH appeared from the nmr spectrum of the acetate **15** to be the same as in the lactol **5** and its derivatives.[3] Accompanying the lactol in the lithium aluminum tri-*tert*-butoxyhydride reduction product were traces of the lactone **7**, detected by tlc, and a further compound, not obtained in sufficient quantity for isolation. Its polarity in tlc indicated that it was probably the lactol **14**, which is supported by the reduction of a mixture with the lactone **7** by ethanolic sodium borohydride to a mixture of the lactones **7** and **8**. These results show that lithium aluminum tri-*tert*-butoxyhydride also reduces the anhydride **6** with high selectivity, which further supports the mechanistic postulates made above, since with this extremely bulky attacking anion the reduction takes place almost exclusively of the *more* hindered carbonyl of the substrate. The variability of these anhydride reductions is potentially useful in the design of syntheses of a variety of natural products.

Experimental Section

General experimental directions are given in ref 3.

Methylation of the Hydroxy Dimethyl Ester 2.—Ethereal diazomethane was gradually added at 0° (N_2) to a solution of the hydroxy dimethyl ester **9** (13 g) in anhydrous ether (250 ml) containing aluminum chloride (0.2 g) until the yellow color persisted. Further aluminum chloride (0.2 g) was then added and the solution stirred at 0° for 30 min. Excess diazomethane was destroyed by dropwise addition of acetic acid, and 2 *N* HCl was then added. The ether layer was dried (Na_2SO_4) and concentrated to an oil, which crystallized from a concentrated solution in methanol, giving the methoxy dimethyl ester **10** (12 g) as stout prisms: mp 92–93°; $[\alpha]^{23}D$ −54° (*c* 1.0, $CHCl_3$); ir ν^{KBr} 1748 cm^{-1} (ester C=O); nmr τ 3.76, 4.01 (2 H, AB q, J = 8 Hz, C-6, C-7 H), 4.85 (2 H, m, C-22, C-23 H), 6.45, 6.55 (3 H each, singlets, $COOCH_3$), 6.63, 7.21 (2 H, AB q, J = 10 Hz, C-1′, C-2′ H), 6.73 (3 H, singlet, C-3 OCH_3), 8.96 (3 H, s, C-19 CH_3), 9.23 (3 H, s, C-18 CH_3). *Anal.* Calcd for $C_{33}H_{54}O_5$: C, 75.77; H, 9.81. Found: C, 75.67; H, 9.88.

Synthesis of the Methoxy Anhydride 6.—The methoxy dimethyl ester **10** (6g) was dissolved in warm propylene glycol (90 g) (N_2), and after gradual addition of 50% aqueous potassium hydroxide (17.4 g) the mixture was heated under reflux (N_2) for 3–4 hr. The reaction mixture was poured into a large volume of 2 *N* HCl which caused an acidic product (5.8 g) to be precipitated.

This material (2 g) was heated under reflux with acetic anhydride (15 ml) for 1 hr. Cooling the mixture caused crystallization of the anhydride **6** (1.7 g), essentially pure. One recrystallization from acetic anhydride gave the analytical sample as needles: mp 169–170°; $[\alpha]^{23}D$ −32° (*c* 1.0, $CHCl_3$); ir ν^{KBr} 1850, 1775 cm^{-1} (anhydride C=O); nmr given fully in text. *Anal.* Calcd for $C_{33}H_{48}O_4$: C, 77.91; H, 9.51. Found: C, 77.87; H, 9.37.

Reaction of the Methoxy Anhydride 6 with Sodium Borohydride.—Sodium borohydride (250 mg) was added to a solution of the methoxy anhydride **6** (1.7 g) in freshly distilled dioxane (17 ml) and the mixture heated under reflux for 3 hr. The solution was let cool, diluted with water, and extracted with ether. The ether layer was dried ($MgSO_4$) and concentrated to a clear oil which was chromatographed in benzene on alumina (Fisher, alumina for chromatography, 50 g). Elution with benzene rapidly gave a lactonic fraction (by ir, 0.7 g). This material was chromatographed on two E. Merck 2.0-mm silica gel preparative layer plates. Each plate was developed nine times with pentane–ether (9:1), giving two well-resolved bands (uv visualization). Each band from both dried plates was excised, powdered, and mixed with the equivalent from the other plate. The adsorbents were then exhaustively extracted (Soxhlet) with ether. The ethereal extract of the material from the slower moving band crystallized on concentration to give the methoxy lactone **7** as needles (275 mg): mp 161–163°; $[\alpha]^{23}D$ −87° (*c* 1.0, $CHCl_3$); ORD, negative Cotton effect, $[\alpha]_{MeOH}$ −4200° at 215 nm, the first extreme; λ_0 208 nm; CD, negative, trough not observable under the conditions employed; ir ν^{KBr} 1760 cm^{-1} (γ-lactone); nmr given in text. *Anal.* Calcd for $C_{33}H_{50}O_3$: C, 80.11; H, 10.19. Found: C, 80.30; H, 10.17. (Note that the ORD data for the acetoxy lactone **2** were incorrectly given in ref 3; the correct data are $[\alpha]_{MeOH}$ −3900° at 220 nm, the first extreme; λ_0 208 nm). The ethereal extract of the faster moving band also crystallized on concentration to give the methoxy lactone **8** as needles (290 mg): mp 168–170.5°; $[\alpha]^{23}D$ −9° (*c* 1.0, $CHCl_3$); ORD, positive followed by negative Cotton effects, peak at 230 nm, $[\alpha]_{MeOH}$ +200°, trough at 209 nm, $[\alpha]_{MeOH}$ −3450°; λ_0 224 nm; CD, positive Cotton effect, peak at 229 nm, $[\theta]_{MeOH}$ +5000°; ir ν^{KBr} 1750 cm^{-1} (γ-lactone); nmr given in text. *Anal.* Calcd for $C_{33}H_{50}O_3$: C, 80.11; H, 10.19. Found: C, 80.23; H, 10.10.

Methylation of the Hydroxy Lactone 12 to the Methoxy Lactone 7.—To a solution of the hydroxy lactone **12** (50 mg) in anhydrous

ether (10 ml) at 0°, anhydrous aluminum chloride (10 mg) was added, followed by excess ethereal diazomethane, until the yellow color persisted briefly. Further aluminum chloride and diazomethane solution were then added. After 30 min of stirring at 0°, glacial acetic acid was added dropwise to destroy excess diazomethane. Work-up as in the methylation of **9** described above gave a material shown by tlc to comprise the methoxy lactone **7** and a small amount of the hydroxy lactone **12**. No methoxy lactone **8** was observed.

Reductions of Lactone 7 and 8 with Lithium Aluminum Hydride.—The lactone **7** (50 mg) was heated under reflux in dioxane (5 ml) with lithium aluminum hydride (10 mg) for 4 hr. The reaction was quenched with aqueous dioxane and worked up *via* 2 *N* HCl and ether. The product was the methoxy diol **11** (20 mg), which crystallized from ethyl acetate–hexane as needles: mp 190.5–191.5°; $[\alpha]^{23}D$ −60° (*c* 1.0, $CHCl_3$); ν^{KBr} 3400 cm^{-1} (OH). *Anal.* Calcd for $C_{33}H_{54}O_3$: C, 79.46; H, 10.92. Found: C, 79.32; H, 10.90.

Lactone **8**, reduced in the same way, gave the same methoxydiol.

Reductions of the Methoxy Anhydride 6 with Lithium Aluminum Hydride and Sodium Aluminum Hydride. 1. With Lithium Aluminum Hydride.—A solution of the methoxy anhydride **6** (500 mg) in tetrahydrofuran (5 ml) was added dropwise to a stirred solution of lithium aluminum hydride (40 mg) in tetrahydrofuran (5 ml) at −55° (acetone–CO_2 bath). The mixture was let warm to −5° during 90 min and stirred at this temperature for 30 min, after which it was acidified (6 *N* HCl) and partitioned between water and ether. The organic material obtained by concentration of the dried (Na_2SO_4) ether layer was chromatographed as described for the reduction of **6** with sodium borohydride above. Lactones **7** and **8** were obtained pure in yields of 200 and 15 mg, respectively. They were identified by tlc and ir.

2. With Sodium Aluminum Hydride.—From 525 mg of anhydride **6** and 100 mg of sodium aluminum hydride (Ventron), lactone **7** and **8** were obtained in yields of 275 and 30 mg, respectively, using the same procedure as above.

Reduction of the Methoxy Anhydride 6 with Lithium Aluminum Tri-*tert*-butoxyhydride.—A solution of the anhydride **6** (1 g) in tetrahydrofuran (25 ml) was added dropwise to a stirred solution of lithium aluminum tri-*tert*-butoxyhydride (2.0 g) in tetrahydrofuran (25 ml) at 0°. After 5 hr at 0°, the reaction was quenched with excess 2 *N* HCl, and the mixture partitioned between water and ether. The ether layer was dried ($MgSO_4$) and concentrated, and the organic product chromatographed on preparative silica gel plates as in experiments described above, except that pentane–ethyl acetate (10:1) was used as developing solvent. After four developments, three bands were discerned: one at the origin and two above it. Extraction of the lower two of these as above gave the same material which was the lactol **13**, obtained from ether as fine needles (650 mg): mp 234–237° dec; $[\alpha]^{23}D$ −51° (*c* 1.0, $CHCl_3$); ir ν^{KBr} 3404, 3230 (OH), 1770 (γ-lactone), 1735 cm^{-1} (aldehyde and acid C=O); ν^{CHCl_3} 3300 (OH), 1765 cm^{-1} (γ-lactone). *Anal.* Calcd for $C_{33}H_{50}O_4$: C, 77.60; H, 9.87. Found: C, 77.68; H, 9.69. Treatment of this compound (50 mg) with acetic anhydride (2 ml) under reflux (N_2) for 3 hr and removal of solvent under reduced pressure gave a slowly crystallizing oil, which after two recrystallizations from ethyl acetate–hexane gave the pure lactol acetate **15** as needles: mp 170–172°; ir ν^{KBr} 1780 (γ-lactone C=O), 1755 cm^{-1} (lactol acetate C=O); nmr τ 3.69, 4.12 (2 H, AB quartet, J = 10 Hz, C-6, C-7 H), 3.87 (1 H, broadened singlet, C-3′ H), 4.82 (2 H, m, C-22, CH23 H), 6.63 (3 H, singlet, C-3 OCH_3), 7.85 (3 H, singlet, lactol CH_3COO), 8.91 (3 H, singlet, C-19 CH_3), 9.24 (3 H, singlet, C-18 CH_3). *Anal.* Calcd for $C_{35}H_{52}O_5$: C, 76.04; H, 9.48. Found: C, 76.13; H, 9.50. The highest band in the preparative tlc from the reduction was present in very small amount. Analytical tlc of this band showed it to contain two compounds, one identical with the methoxy lactone **7**. Reduction of a very small sample of this mixture with sodium borohydride in ethanol and work-up as above gave (tlc) a mixture containing methoxy lactone **7** and **8** only.

Similar sodium borohydride reduction of the pure lactol **13** gave the methoxy lactone **7**.

Registry No.—**1**, 30345-18-7; **2**, 30345-11-0; **6**, 30345-12-1; **7**, 30345-13-2; **8**, 30409-20-2; **10**, 30345-14-3; **11**, 30345-15-4; **13**, 30345-16-5; **15**, 30345-17-6.

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Steroids. VIII.[1] A-Nor Steroids *via* Pinacol-Type Rearrangement

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Pinacol-type rearrangement of 2α-hydroxy-3α-mesyloxy-2β-methylcholestane led to 2β-acetyl-1-norcholestane, the structure and stereochemistry of which was confirmed by Baeyer–Villiger oxidation to the known 2β-acetoxy-*A*-norcholestane and subsequent saponification and oxidation to the known *A*-norcholestan-2-one. Analogous rearrangement of 3β-hydroxy-4β-mesyloxy-3α-methyl-5β-cholestane gave 3ξ-acetyl-*A*-nor-5β-cholestane.

In the course of a synthesis of steroids with modified ring systems,[2] it was necessary to contract the A ring of certain steroids and introduce the progesterone side chain. The synthesis of A-nor steroids has been effected previously through the Favorskii reaction or the benzilic acid rearrangement.[3–7] Since these methods were not particularly suited to our objectives, a pinacol-type rearrangement was studied. This approach has been used for the modification of the D ring of steroids.[8,9] After the completion of our work, the preparation of A-homo-B-nor and A-nor-B-homo steroids[10] and ring-contracted pinane derivatives[11] through a pinacol-type rearrangement was described.

Reaction of 3-cholestanone with methylmagnesium bromide gave a tertiary alcohol which could be dehydrated readily[12] to an olefin **1**. The nmr spectrum of **1**

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