2. *Reactions of Ketones with Oxidising Agents. Part II.*[1] *Acetoxylation of* 11- *and* 20-*Oxo-steroids with Lead Tetra-acetate in the Presence of Boron Trifluoride.*

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Pregnan-20-ones and pregnane-11,20-diones react with lead tetra-acetate at 25° in the presence of boron trifluoride to give the corresponding 21-acetoxy-compounds in good yield. Acetoxylation of a pregnan-11-one was slower, but at 50° the 9α-acetoxy-11-oxo-compound (15%) was obtained.

In Part I of this series [1] it was shown that cholestan-2- and -3-one were acetoxylated by lead tetra-acetate at room temperature when boron trifluoride was present as catalyst. We have now extended this reaction to 11- and 20-oxo-steroids.

The 21-acetoxylation of 20-oxo-steroids with lead tetra-acetate in acetic acid and acetic anhydride has been reported to give yields ranging from 3% (from progesterone [2]) to 62% (from 3α,11α-diacetoxy-5α-pregnan-20-one [3]). Using the method described in the literature (24 hr. at 70°) we obtained 42% of the 21-acetoxy-compound (II; R = Ac) from 3β-acetoxy-5α-pregnane-11,20-dione (I; R = Ac). Higher yields (50—60%) were obtained when the boron trifluoride–ether complex was present and the reaction was complete in 2 hr. at 25°.

The best yield (86%) of 21-acetoxy-compound (II; R = Ac) was obtained when 5% methanol in benzene was used as solvent for a boron trifluoride-catalysed reaction at room temperature. It is possible that under these conditions the boron trifluoride is converted [4] into the protonic acid $H^+[MeOBF_3]^-$. Benzene–acetic acid was a less satisfactory solvent (23% yield) and no 21-acetoxy-compound was isolated when benzene alone was used as solvent.

With 3α-hydroxy-5β-pregnane-11,20-dione the best yield (70%) was again achieved with the boron trifluoride-catalysed reaction in benzene–methanol, the 3-hydroxy-group being unaffected. In benzene the yield was <4% after 23 hr., some lead tetra-acetate remaining, whereas in methanol all the reagent was consumed in 2 hr., and the product contained <1% of 21-hydroxy- or 21-acetoxy-20-ketone.

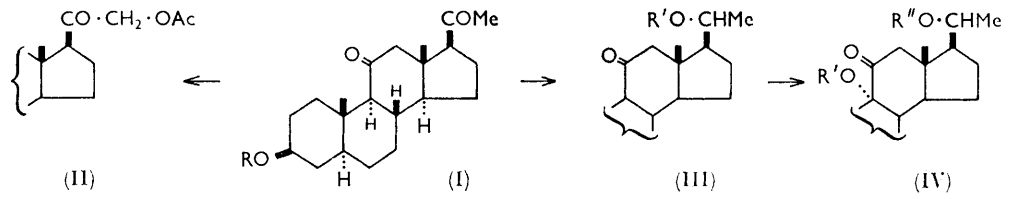
Attempts to use other Lewis acids were unsuccessful in benzene or benzene–methanol. Precipitates were formed, apparently as a results of reactions between lead tetra-acetate and the Lewis acids. With acetic acid as solvent, proton acids did not catalyse the acetoxylation efficiently. Less than 7% of 21-acetoxy-20-ketone was formed, and there was concomitant partial acetylation of the 3-hydroxy-group.

[1] Part I, Henbest, Jones, and Slater, *J.*, 1961, 4472.
[2] Reichstein and Montigel, *Helv. Chim. Acta*, 1939, **22**, 1212.
[3] Sondheimer, Rosenkranz, Mancera, and Djerassi, *J. Amer. Chem. Soc.*, 1953, **75**, 2601.
[4] Nieuwland, Vogt, and Foohey, *J. Amer. Chem. Soc.*, 1930, **52**, 1018.

Acetoxylation with lead tetra-acetate and boron trifluoride in benzene–methanol has also been applied successfully to 5α-pregnane-11,20-dione, 3α-hydroxy-5β-pregnan-20-one, 3α-acetoxy-5β-pregnane-11,20-dione, and 3β-acetoxy-16α,17α-epoxy-5α-pregnane-11,20-dione. The reaction was unsuccessful with 3β-acetoxy-16α,17α-epoxy-16β-methyl-5α-pregn-9-en-20-one, which underwent enlargement of ring D. With unsaturated steroids lower yields are to be expected, but the results were better than those from uncatalysed reactions. Thus, progesterone gave 11% of deoxycorticosterone acetate (lit.,[2] 3%), and pregnenolone furnished 43% of 21-acetoxy-compound (lit.,[2] 17% for the acetoxylation of pregnenolone acetate).

With pregnane-11,20-diones there was no evidence for acetoxylation adjacent to the 11-oxo-group. This relative unreactivity of the 11-oxo-group was confirmed by a study of the acetoxylation of 3β,20β-diacetoxy-5α-pregnan-11-one (III; R = R′ = Ac), which was prepared from 3β-acetoxy-5α-pregnane-11,20-dione (I; R = Ac) by reduction with sodium borohydride in methanol and subsequent acetylation. With this 11-ketone the rate of consumption of lead tetra-acetate was much lower than with 3- or 20-ketones. After 13·5 hr. at 50° in benzene–methanol containing boron trifluoride only a 3% yield of a mono-acetoxylated product was obtained. The same compound was obtained in 15% yield from a reaction at 50° in acetic acid, and it is formulated as the 9α-acetoxy-compound (IV; R = R′ = R″ = Ac) on the following evidence. All three acetate-groups were hydrolysed by alkali, and the resultant triol (IV; R = R′ = R″ = H) gave only a diacetate (IV; R = R″ = Ac, R′ = H) on acetylation with acetic anhydride–pyridine. Under more vigorous conditions it gave the original triacetate (IV; R = R′ = R″ = Ac), albeit in low yield, together with a contaminant which, from its ultraviolet absorption, could have been a Δ^8-11-ketone. The difficulty of esterifying the third hydroxy-group is consistent with its being tertiary (9α). The triol (IV; R = R′ = R″ = H) was diacetylated by bismuth oxide in acetic acid. A 12-hydroxy-11-ketone should have been oxidised to a diketone.[5]

The $\Delta[M]_D$ (+120°) for introduction of the third hydroxy-group into the diol (III; R = R′ = H) is of the same order as that for the introduction of a 9α-hydroxy-group into 3β-acetoxy-17α-hydroxy-5α-pregnane-11,20-dione (+126°) and 3β-acetoxy-5α-ergostan-11-one (+95°).[6]

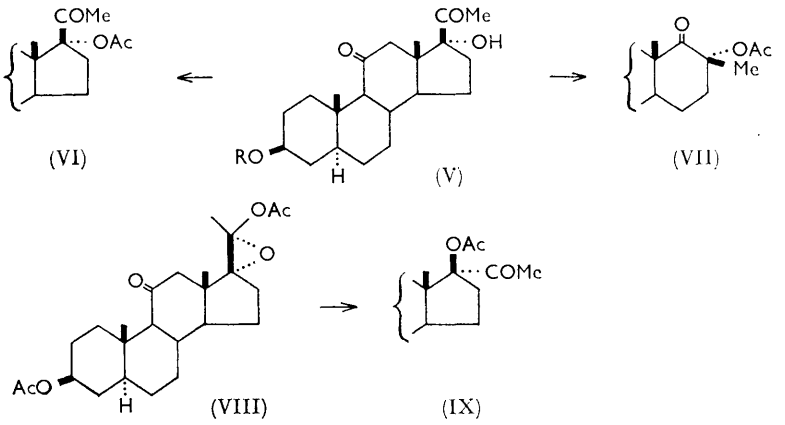


The proton magnetic resonance spectrum of the triacetate (IV; R = R′ = R″ = Ac), when compared with that of the diacetate (III; R = R′ = Ac), showed a new peak assigned to the introduced acetoxy-group. Both compounds showed a sharp peak (τ *ca.* 7·6) ascribed to the two protons at the 12-position,[7] and only two-proton resonance at a chemical shift appropriate to the >C*H*·OAc group. These observations exclude substitution at the 12-position and confirm the tertiary nature of the introduced acetoxy-group.

A by-product was isolated from the reaction of 3β-acetoxy-5α-pregnane-11,20-dione with lead tetra-acetate and boron trifluoride in the presence of acetic acid. It gave

[5] Rigby, *J.*, 1951, 793.
[6] Barton, Evans, Hamlet, Jones, and Walker, *J.*, 1954, 747.
[7] Shoolery and Rogers, *J. Amer. Chem. Soc.*, 1958, **80**, 5121; Cox, Bishop, and Richards, *J.*, 1960, 5118.

analyses for a monoacetoxy-derivative and differed from the 17α-acetoxy-compound (VI; R = Ac) and the D-homo-compound (VII; R = Ac). These were prepared from 3β,17α-dihydroxy-5α-pregnane-11,20-dione (V; R = H) by reaction with acetic anhydride, catalysed by toluene-*p*-sulphonic acid, and boron trifluoride, respectively.[8] It also differed from the known 3β,12β-diacetoxy-5α-pregnane-11,20-dione [9] and 3β,21-diacetoxy-5α,17α-pregnane-11,20-dione.[10] The $\Delta[M]_D$ for the introduction of the new



acetoxy-group was −307°, whereas that for introduction of a 9α-acetoxy-group into the 20β-acetoxy-compound (III; R = Ac) described above was +44°; formulation of the by-product as the 9α-acetoxy-derivative therefore seemed unlikely. It was identified as the 17β-acetoxy-17α-pregnan-20-one (IX), prepared by thermal rearrangement [11] of the epoxide (VIII).

In the proton magnetic spectra of the 17-epimers (VI; R = Ac) and (IX) the most significant difference was in the position of the 13-methyl peak, which occurred at τ 9·44 in the 17α-acetoxy-compound (VI) and at τ 9·08 in the 17β-acetoxy-compound (IX). A similar difference was observed in the spectra of 3β,17α-diacetoxy-16β-methyl-5α-pregn-9-en-20-one (τ 9·40 for 13-methyl) and its 17-epimer (τ 9·08).[12]

The mechanism of formation of the 17β-acetoxy-17α-pregnan-20-one is not clear, but a 16β-acetoxy-17-ketone was obtained from the enol acetate of a 17-ketone with lead tetra-acetate,[13] perhaps by an analogous mechanism.

Experimental

M. p.s were determined on a Kofler hot-stage apparatus. Rotations were determined for chloroform solutions. Proton magnetic resonance spectra were determined for *ca.* 6% solutions in deuteriochloroform.[14]

Acetoxylation of 3β-Acetoxy-5α-pregnane-11,20-dione (I; R = Ac).—The diketone (0·5 g., 1 mol.) and lead tetra-acetate (0·65 g., 1·1 mol.) in a mixture of benzene (19 ml., 160 mol.) and methanol (1 ml., 19 mol.) containing the boron trifluoride–ether complex (2·5 ml., 15 mol.) was stirred at 25°. After 3 hr. the starch–iodide test for lead tetra-acetate was negative. The product, after isolation with ether, was dissolved in benzene–light petroleum (1 : 4), from which 3β,21-diacetoxy-5α-pregnane-11,20-dione (II; R = Ac) (497 mg., 86%) separated; it

[8] Turner, *J. Amer. Chem. Soc.*, 1952, **74**, 4220.
[9] Martinez, Ringold, Rosenkranz, and Djerassi, *J. Amer. Chem. Soc.*, 1953, **75**, 239.
[10] Shoppee and Reichstein, *Helv. Chim. Acta*, 1940, **23**, 729.
[11] Soloway, Considine, Fukushima, and Gallagher, *J. Amer. Chem. Soc.*, 1954, **76**, 2941.
[12] Attenburrow, Connett, Graham, Oughton, Ritchie, and Wilkinson, *J.*, 1961, 4547.
[13] Johnson, Gastamtide, and Pappo, *J. Amer. Chem. Soc.*, 1957, **79**, 1991.
[14] Green, Page, and Staniforth, *J.*, 1964, 144.

had m. p. 142—144° (lit.,[10] m. p. 143—147°) and its infrared spectrum was identical with that of an authentic sample.

The following Table gives a summary of the reactions carried out between the diketone (1 mol.), lead tetra-acetate (1·1 mol.), and catalyst (15 mol.) under various conditions. In some experiments, the product was examined by chromatography. Thus, crystallisation (benzene–light petroleum) of the total product from the reaction in benzene–acetic acid gave only 100 mg. of the acetate (II; R = Ac). The remainder was chromatographed on deactivated alumina (50 g.). Elution with benzene–light petroleum (1 : 4) yielded a gum which crystallised from ethanol to give 3β,17β-*diacetoxy*-5α,17α-*pregnane*-11,20-*dione* (IX) (see below) (74 mg.), m. p. 241—242°, $[\alpha]_D$ +10° (Found: C, 69·4; H, 8·3. $C_{25}H_{36}O_6$ requires C, 69·4; H, 8·4%). Elution with benzene gave the acetate (II; R = Ac) (440 mg.), m. p. 142—145°.

Acetoxylation of 3β-acetoxy-5α-pregnane-11,20-dione.

Steroid (g.)	Solvent (mol.)	Temp.	Reaction time (min.)	Yield of 21-acetate
1	C_6H_6 (87)	25°	110	None isolated
2	C_6H_6 (160) + AcOH (13)	25	180	540 mg.; 23% *†
0·5	C_6H_6 (172) + MeOH (15)	25	180	497 mg.; 86% *
2	AcOH (65)	25	60	1·1 g.; 45% *§
1	AcOH (130)	25	80	661 mg.; 57% *
2	AcOH (130)	25	180	250 mg.; 22% †‡
1	AcOH (260)	25	135	671 mg.; 58% *
0·5	AcOH (177) + Ac_2O (1·8)	70	34 hr.	245 mg.; 42% †

* Isolation by crystallisation. † Isolation by chromatography and crystallisation. ‡ These experiments also gave 3β,17β-diacetoxy-5α,17α-pregnane-11,20-dione (3 and 5%, respectively). § Starting material (10%) was also obtained.

Acetoxylation of 3α-*Hydroxy*-5β-*pregnane*-11,20-*dione*.—The diketone (8·77 g., 1 mol.) and lead tetra-acetate (13·34 g., 1·14 mol.) were stirred in a mixture of benzene (370 ml.) and methanol (20 ml.) and treated with the boron trifluoride–ether complex (50 ml.). After 4 hr. at 24° a starch–iodide test was negative and the product was isolated with chloroform and crystallised from ethyl acetate–light petroleum (b. p. 60—80°), to give 21-acetoxy-3α-hydroxy-5β-pregnane-11,20-dione (6·72 g., 65·5%), m. p. 135—138°. A second crop was recrystallised, giving more of the 21-acetate (0·54 g., 5%), m. p. 137—139° (lit.,[15] m. p. 137—138°).

The following Table gives a summary of the reactions carried out between the diketone (1·0 g., 1 mol.) and lead tetra-acetate (1 mol.) at room temperature with Lewis acids (13·3 mol.) or proton acids (3·3 mol.) as catalyst. The products were isolated when a starch–iodide test became negative or after *ca.* 23 hr. if it remained positive. The crude products were analysed for ketols by the tetrazolium method, with cortisone acetate as standard.

Acetoxylation of 3α-hydroxy-5β-pregnane-11,20-dione.

Solvent (mol.)	Catalyst	Reaction time (hr.)	Starch-iodide test	Ketol (%)
C_6H_6 (142)	$BF_3{\cdot}Et_2O$ *†	23	+	4
C_6H_6 (142) + MeOH (17)	$BF_3{\cdot}Et_2O$ *†	4	—	65
C_6H_6 (112) + MeOH (84)	,,	2	—	14
MeOH (337)	,,	2	—	<1
AcOH (117)	*p*-Me·C_6H_4·SO_3H *	6	—	4
AcOH (117)	Concn. H_2SO_4	6	—	7
AcOH (117)	HBr	23	+	1

* In the absence of catalyst <1% of ketol was produced. † <2% of ketol was produced with 13·3 mol. of $SnCl_4$, $ZnCl_2$, or $AlCl_3$ instead of BF_3,Et_2O.

21-*Acetoxy*-5α-*pregnane*-11,20-*dione*.—5α-Pregnane-11,20-dione (2·19 g.) was stirred for 4 hr. at room temperature with lead tetra-acetate (3·3 g.) in benzene (95 ml.) and methanol (5 ml.) containing the boron trifluoride–ether complex (12·7 ml.). The product, isolated with benzene, crystallised from ethyl acetate to give 21-*acetoxy*-5α-*pregnane*-11,20-*dione* (1·52 g.,

[15] Von Euw, Lardon, and Reichstein, *Helv. Chim. Acta*, 1944, **27**, 1287.

59%), m. p. 158—161°. Recrystallisation from ethyl acetate gave a sample, m. p. 161·5—163·5°, $[\alpha]_D$ +111° (Found: C, 73·4; H, 9·1. $C_{23}H_{34}O_4$ requires C, 73·8; H, 9·15%).

21-*Acetoxy*-3α-*hydroxy*-5β-*pregnan*-20-*one*.—3α-Hydroxy-5β-pregnan-20-one (3·18 g.) was stirred for 4 hr. at room temperature with lead tetra-acetate (4·65 g.) in benzene (127 ml.) and methanol (6·5 ml.) containing the boron trifluoride–ether complex (18·6 ml.). The product, isolated with benzene, crystallised from ethyl acetate–light petroleum (b. p. 60—80°), to give the 21-acetoxy-compound (2·4 g., 64%), m. p. 167—171°. After recrystallisation it had m. p. 173—176°, $[\alpha]_D$ +109° (lit.,[16] m. p. 179·5—181°, $[\alpha]_D$ +109·4°).

3α,21-*Diacetoxy*-5β-*pregnane*-11,20-*dione*.—3α-Acetoxy-5β-pregnane-11,20-dione (498 mg.) was stirred for 4 hr. at 23° with lead tetra-acetate (652 mg.) in benzene (19 ml.) and methanol (1 ml.) containing the boron trifluoride–ether complex (2·5 ml.). The product, isolated with chloroform, crystallised from ethyl acetate–light petroleum (b. p. 40—60°) as prisms (271 mg., 47%), m. p. 106—109°, $[\alpha]_D$ +125° (lit.,[17] m. p. 107—109°, $[\alpha]_D$ +123°).

3β,21-*Diacetoxy*-16α,17α-*epoxy*-5α-*pregnane*-11,20-*dione*.—3β-Acetoxy-16α,17α-epoxy-5α-pregnane-11,20-dione (2·0 g.) was stirred for 5 hr. with lead tetra-acetate (2·5 g.) in benzene (76 ml.) and methanol (4 ml.) containing the boron trifluoride–ether complex (10 ml.). The product, isolated with benzene, was crystallised twice from benzene–light petroleum, to give the 3β,21-*diacetate* (490 mg., 21%), m. p. 181—183·5°, $[\alpha]_D$ +81° (Found: C, 67·2; H, 7·7. $C_{25}H_{34}O_7$ requires C, 66·9; H, 7·65%), $\nu_{max.}$ (in CS_2) 1756 and 1224 (21-OAc), 1736 and 1242 (3-OAc), 1708 (ketone) and 898 and 834 $cm.^{-1}$ (epoxide).

21-*Acetoxypregn*-4-*ene*-3,20-*dione*.—Progesterone (418 mg.) was stirred for 4 hr. at room temperature with lead tetra-acetate (652 mg.) in benzene (19 ml.) and methanol (1 ml.) containing the boron trifluoride–ether complex (2·5 ml.). The product, isolated with benzene, was crystallised twice from ethyl acetate–light petroleum (b. p. 40—60°) to give the 21-acetoxy-compound (56 mg., 11%), m. p. 153—157°, $\lambda_{max.}$ (in EtOH) 239·5 mμ (ε 16,100) (lit.,[2] m. p. 158—160°).

21-*Acetoxy*-3β-*hydroxypregn*-5-*en*-20-*one*.—3β-Hydroxypregn-5-en-20-one (841 mg.) was stirred for 4 hr. at room temperature with lead tetra-acetate (1·304 g.) in benzene (38 ml.) and methanol (2 ml.) containing the boron trifluoride–ether complex (5 ml.). The product, isolated with benzene, was crystallised twice from ethyl acetate to give the 21-acetoxy-compound (425 mg., 43%), m. p. 177·5—181°, $[\alpha]_D$ +35° (lit.,[18] m. p. 184—185°).

3β,20β-*Diacetoxy*-5α-*pregnan*-11-*one* (III; R = R′ = Ac).—3β-Acetoxy-5α-pregnane-11,20-dione (1·87 g.) was reduced with sodium borohydride (0·29 g., 1·5 mol.) in methanol (374 ml.) at 0° for 1 hr. Acetic acid (1 ml.) was added and the solution was evaporated to dryness. Water and ethyl acetate were added; the ethyl acetate layer was evaporated and the residue crystallised from methanol to give 3β-*acetoxy*-20β-*hydroxy*-5α-*pregnan*-11-*one* (III; R = H, R′ = Ac) (1·14 g., 60%), m. p. 192—193°, $[\alpha]_D$ +19° (Found: C, 73·55; H, 9·75. $C_{23}H_{36}O_4$ requires C, 73·35; H, 9·65%). Acetylation afforded 3β,20β-diacetoxy-5α-pregnan-11-one (III; R = R′ = Ac) m. p. 158—161°, $[\alpha]_D$ +34°, τ 5·17 and 5·33 (3α-H and 20-H), 7·64 (12-H_2), 7·96 (3- and 20-acetoxy), 8·82 and 8·95 (21-H_3 and 19-H_3) and 9·40 (18-H_3) (lit.,[19] m. p. 155—157°, $[\alpha]_D$ +33°).

Acetoxylation of 3β,20β-*Diacetoxy*-5α-*pregnan*-11-*one*.—The diacetoxy-11-ketone (544 mg., 1 mol.) and lead tetra-acetate (634 mg., 1·1 mol.) in acetic acid (22·23 ml., 300 mol.) containing the boron trifluoride–ether complex (0·96 ml., 5·9 mol.) was stirred at 50° for 25 hr. (negative starch–iodide test). The product, which contained no appreciable amount of αβ-unsaturated ketone, was chromatographed on deactivated alumina (17·6 g.). Elution with pentane–benzene (3 : 1) gave starting material (125 mg., 23%), m. p. 157—160°. Elution with benzene afforded 3β,9α,20β-*triacetoxy*-5α-*pregnan*-11-*one* (IV; R = R′ = R″ = Ac) (95 mg., 15%), m. p. 236—239°, $[\alpha]_D$ +39° (Found: C, 68·05; H, 8·3. $C_{27}H_{40}O_7$ requires C, 68·05; H, 8·45%), τ 5·28 and 5·45 (3α-H and 20-H), 7·53 (12-H_2), 7·80 (9α-OAc), 7·96 (3- and 20-OAc), 8·80 and 8·87 (19-H_3 and 21-H_3), and 9·39 (18-H_3). A non-crystalline intermediate fraction (82 mg.) was also obtained. Use of benzene or benzene–methanol (30 : 1) at 50° gave lower yields (3—5%) of the triacetate.

Reactions of 3β,9α,20β-*Triacetoxy*-5α-*pregnan*-11-*one* (IV; R = R′ = R″ = Ac).—Alkaline

[16] Reichstein and Fuchs, *Helv. Chim. Acta*, 1940, **23**, 658.
[17] Norymberski, *J.*, 1956, 517.
[18] Steiger and Reichstein, *Helv. Chim. Acta*, 1937, **20**, 1164.
[19] Romo, Stork, Rosenkranz, and Djerassi, *J. Amer. Chem. Soc.*, 1952, **74**, 2918.

hydrolysis gave a triol, m. p. 202—205° (no C=O present); this compound (57 mg.) and bismuth oxide (152 mg., 2 mol.) in AnalaR acetic acid were heated at 118° for 24 hr.; no bismuth was precipitated. Crystallisation of the product from methanol–acetone yielded 3β,20β-*diacetoxy*-9α-*hydroxy*-5α-*pregnan*-11-*one* (IV; R = R″ = Ac; R′ = H), m. p. 218—220°. A purer sample, m. p. 222—223°, $[\alpha]_D$ +58° (Found: C, 69·4; H, 9·0. $C_{25}H_{38}O_6$ requires C, 69·1; H, 8·8%), was obtained by treatment of the triol with acetic anhydride–pyridine at 40° for 18 hr. Attempted oxidation of the diacetoxy-ketol with chromic acid led to recovery of the starting material.

The diacetoxy-ketol was recovered after treatment with acetic anhydride containing toluene-*p*-sulphonic acid at 40° overnight. Acetylation was achieved by boiling the compound (133 mg.) in chloroform (10 ml.), acetyl chloride (2 ml.), and dimethylaniline (5 ml.) for 17 hr. The product was chromatographed in pentane–benzene (3 : 1) on deactivated alumina (8 g.). Elution with pentane–benzene (3 : 1) gave an oil (88 mg.) containing αβ-unsaturated ketone ($\nu_{max.}$ 1665 cm.$^{-1}$). Elution with benzene yielded 3β,9α,20β-triacetoxy-5α-pregnan-11-one (10 mg., 7%), m. p. and mixed m. p. 236—238°, followed by starting material (20 mg., 15%), m. p. and mixed m. p. 221—223°.

3β,20α-*Diacetoxy*-5α-*pregnan*-11-*one*.—Sodium (3 g., 10 atom-equiv.) was added gradually to a boiling solution of 3β-hydroxy-5α-pregnane-11,20-dione (1·11 g.) in ethanol (250 ml.). The product was acetylated at 20° and the resulting material chromatographed on deactivated alumina (37 g.). Elution with pentane–benzene (1 : 1) gave 3β,20α-*diacetoxy*-5α-*pregnan*-11-*one* (0·1 g., 7%), m. p. 184—186°, $[\alpha]_D$ −37° (Found: C, 71·6; H, 9·3. $C_{25}H_{38}O_5$ requires C, 71·75; H, 9·15%). Further elution with pentane–benzene afforded 3β-acetoxy-5α-pregnane-11,20-dione (0·52 g., 42%), m. p. and mixed m. p. 128—130°.

3β,17α-*Diacetoxy*-5α-*pregnane*-11,20-*dione* (VI; R = Ac).—A solution of 3β,17α-dihydroxy-5α-pregnane-11,20-dione (250 mg.) and toluene-*p*-sulphonic acid (250 mg.) in acetic acid (12·5 ml.) and acetic anhydride (2·5 ml.) was kept at 20° for 3 hr. Addition of water gave a solid that was crystallised from di-isopropyl ether to give the 3β,17α-*diacetate* (VI; R = Ac) (238 mg., 77%), m. p. 222—224°, $[\alpha]_D$ +13° (Found: C, 69·4; H, 8·4. $C_{25}H_{36}O_6$ requires C, 69·4; H, 8·4%), $\nu_{max.}$ (in CS_2) 1740 and 1246 (acetates), 1722 (20-ketone) and 1712 cm.$^{-1}$ (ketone), τ 5·33 (3α-H), 7·75 (12-H_2), 7·85 (17-OAc), 7·99 (3-OAc and 21-H_3), 8·98 (19-H_3), and 9·44 (18-H_3).

3β,17α-*Diacetoxy*-17β-*methyl*-D-*homoandrostane*-11,17*a*-*dione* (VII; R = Ac).—A solution of the 3β,17α-diol (550 mg.) in a mixture of acetic anhydride (100 ml.) and the boron trifluoride–ether complex (5 ml.) was kept at 20° for 18 hr. The product was adsorbed on to deactivated alumina (18 g.); elution with benzene gave the D-*homo-compound* (VII; R = Ac) (610 mg., 90%), m. p. 257—258°, $[\alpha]_D$ +61° (Found: C, 69·6; H, 8·5. $C_{25}H_{36}O_6$ requires C, 69·4; H, 8·4%).

3β,17β-*Diacetoxy*-5α,17α-*pregnane*-11,20-*dione* (IX) (with J. Elks).—3β,20-diacetoxy-17α,20α-epoxy-5α-pregnan-11-one was heated for 15 min. at 200—210°. The starting material melted and the product, m. p. 233—235°, solidified. Recrystallisation from acetone then ethanol gave 3β,17β-diacetoxy-5α,17α-pregnane-11,20-dione, m. p. 241—242°, $[\alpha]_D$ +5° (Found: C, 69·7; H, 8·3%), τ 5·34 (3α-H), 7·76 (12-H_2), 7·87, 7·97, and 7·99 (17-OAc, 3-OAc, and 21-H_3), 8·98 (19-H_3), and 9·08 (18-H_3), $\nu_{max.}$ (in CS_2) 1736 and 1245 (acetates) and 1710 cm.$^{-1}$ (ketones). A mixed m. p. with a minor product of the acetoxylation of 3β-acetoxy-5α-pregnane-11,20-dione was undepressed and the behaviour of the two samples on thin-layer chromatography was identical.

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