Stereoselectivity in Reactions involving the Hydrolysis of Acetoxonium Ions

By **Julia Atkin, Ruth E. Gall** (*née* Lack),* and **Arlene M. Slee,** Department of Organic Chemistry, The University of Sydney, Sydney, Australia

trans-2-Acetoxy-*cis*-4-t-butylcyclohexyl tosylate (VIIIa), on treatment with potassium acetate in acetic acid followed by ice–water, gave *cis*-2-acetoxy-*trans*-4-t-butylcyclohexanol (XIa) whilst under thermodynamic control it gave an equilibrium mixture of (XIa) and *cis*-2-acetoxy-*trans*-5-t-butylcyclohexanol (XIb) with the latter predominating.

Similarly, *trans*-2-acetoxy-*trans*-5-t-butylcyclohexyl tosylate (VIIId) on treatment with potassium acetate in acetic acid followed by ice–water gave *cis*-2-acetoxy-*cis*-5-t-butylcyclohexanol (XIIa) whilst under thermodynamic control it gave an equilibrium mixture of (XIIa) and *cis*-2-acetoxy-*cis*-4-t-butylcyclohexanol (XIIb).

Although the cleavage of 2β-19-epoxy-5α-cholestan-3α-yl acetate (IV) with boron trifluoride followed by ice–water gave 3α,19-diacetoxy-5α-cholestan-2α-ol (Va), under thermodynamic control the major product was 2α,19-diacetoxy-5α-cholestan-3α-ol (Vb). Similarly, 4α,5α-epoxy-5α-cholestan-3β-yl acetate (XIII) was cleaved with sulphuric acid in acetone followed by cold water to give 4β-acetoxy-5α-cholestane-3β,5α-diol (XVIa) whereas under thermodynamic conditions the major product was 3β-acetoxy-5α-cholestane-4β,5α-diol (XVIb).

An acetoxonium ion intermediate has been suggested in the conversion of *trans*-2-acetoxycyclohexyl bromide into *cis*-2-acetoxycyclohexanol with silver acetate in the presence of water.[1,2] For the hydrolysis of the *trans*-decalin derivative (I) King and Allbutt[3] showed a stereoselectivity for the axial acetate (IIa) which could be equilibrated to a mixture of the mono-acetates (IIa) and (IIb) under acidic conditions, and presented evidence for an intermediate orthester (III). Recently in these laboratories[4] it was found that cleavage of 3α-acetoxy-2β,19-epoxy-5α-cholestane (IV) with boron trifluoride in acetic anhydride followed by treatment with ice–water gave the 2α-hydroxy-compound (OH equatorial) (Va) *via* the suggested acetoxonium ion (VI). This mono-alcohol (Va) proved an important intermediate leading to the synthesis of 19-norsteroids.[4] This stereoselectivity in the hydrolysis of acetoxonium ions under kinetic control[3] and its possible use in synthesis has prompted further examination of the stereoselectivity of the reaction under both kinetic and thermodynamic control in the t-butylcyclohexane and steroid series.

trans-1,2-Epoxy-4-t-butylcyclohexane (VII) prepared by treatment of *trans*-2-chloro-*trans*-4-t-butylcyclohexanol[5,6] with base, was cleaved with toluene-*p*-sulphonic acid in acetic anhydride to give *trans*-2-acetoxy-*cis*-4-t-butylcyclohexyl tosylate (VIIIa), the

[1] S. Winstein and R. E. Buckles, *J. Amer. Chem. Soc.*, 1942, **64**, 2787.

[2] R. Boschan and S. Winstein, *J. Amer. Chem. Soc.*, 1956, **78**, 4921.

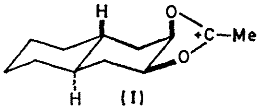
[3] (*a*) J. F. King and A. D. Allbutt, *Tetrahedron Letters*, 1967, 49; (*b*) *Canad. J. Chem.*, 1970, **48**, 1755.

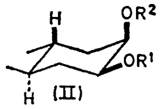
[4] R. E. Lack and A. B. Ridley, *J. Chem. Soc.* (*C*), 1970, 1437.

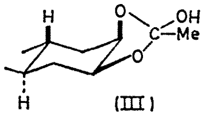
[5] R. F. Czaja and N. A. LeBel, *J. Org. Chem.*, 1961, **26**, 4768.

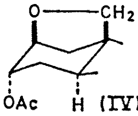
[6] N. L. Allinger, J. Allinger, L. A. Freeberg, R. F. Czaja, and N. A. LeBel, *J. Amer. Chem. Soc.*, 1960, **82**, 5876.

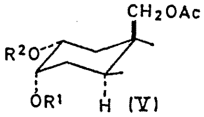
trans-hydroxy-acetate (VIIIb), and the *trans*-diol (VIIIc). The isomeric *trans*-acetoxy-tosylate (VIIId) was isolated by fractional crystallisation of the mixture of isomeric

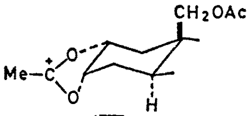

(I)


(II)
a; R[1] = H, R[2] = Ac
b; R[1] = Ac, R[2] = H

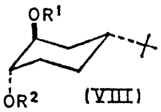

(III)

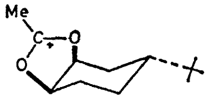

(IV)

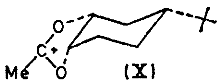

(V)
a; R[1] = Ac, R[2] = H
b; R[1] = H₂, R[2] = Ac
c; R[1] = R[2] = H
d; R[1] = R[2] = Ac

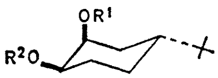

(VI)

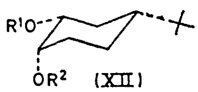

(VII)

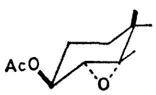

(VIII)
a; R[1] = Ac, R[2] = Ts
b; R[1] = Ac, R[2] = H
c; R[1] = R[2] = H
d; R[1] = Ts, R[2] = Ac
e; R[1] = R[2] = Ac
f; R[1] = H, R[2] = Ac
g; R[1] = H, R[2] = Ts
h; R[1] = Ts, R[2] = H

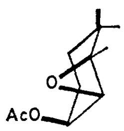

(IX)

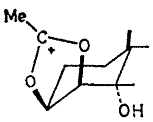

(X)

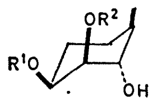

(XI)
a; R[1] = Ac, R[2] = H
b; R[1] = H, R[2] = Ac
c; R[1] = R[2] = Ac


(XII)
a; R[1] = H, R[2] = Ac
b; R[1] = Ac, R[2] = H
c; R[1] = R[2] = Ac
d; R[1] = R[2] = H


(XIII)


(XIV)


(XV)


(XVI)
a; R[1] = H, R[2] = Ac
b; R[1] = Ac, R[2] = H
c; R[1] = R[2] = Ac

acetoxy-tosylates (VIIIa) and (VIIId) obtained when 4-t-butylcyclohexene was treated in acetic anhydride with hydrogen peroxide in the presence of toluene-*p*-sulphonic acid. A mixture would be expected since 4-t-butylcyclohexene gives a mixture of *cis*- and *trans*-epoxides with perbenzoic acid.[7]

Also isolated by preparative t.l.c. were the *trans*-diol (VIIIc), a mixture of the hydroxy-acetates (VIIIb and f), a mixture of the hydroxy-tosylates (VIIIg and h), and the diacetate (VIIIe).

The acetoxy-tosylates (VIIIa) and (VIIId) were each converted into the *trans*-diacetate (VIIIe) by refluxing acetic anhydride in the presence of potassium acetate[8] and this is rationalised by an S_N2 attack by the acetate anion on the acetoxonium ions (IX) and (X) respectively. No reaction occurred in the absence of potassium acetate. The acetoxy-tosylates (VIIIa) and (VIIId), when separately heated with glacial acetic acid and potassium acetate and the mixtures poured onto ice, gave the *cis*-mono-acetates (XIa) and (XIIa) respectively (OH equatorial) with none of the alternative mono-acetates (XIb) and (XIIb). In both cases some of the *trans*-diaxial diacetate (VIIIe) was obtained.

Treatment of the acetoxy-tosylate (VIIIa) with aqueous acetic acid containing potassium acetate under reflux for 4 h gave a mixture of the *cis*-acetoxy-alcohols (XIa) and (XIb) in the ratio 3 : 5 when isolated by preparative t.l.c., together with some of the *cis*-diacetate (XIc). Similar treatment of the acetoxy-tosylate (VIIId) gave a mixture of the *cis*-acetoxy-alcohols (XIIa) and (XIIb) in the ratio 3 : 5 with some of the *cis*-diacetate (XIIc) and the *cis*-diol (XIId).

The products were identified by their n.m.r. spectra (Table 1) in which the protons α to the acetoxy-group

TABLE 1

N.m.r. data in the t-butylcyclohexane series

	Proton α to tosylate		Proton α to acetate		Proton α to hydroxy		
Compd.	τ	W_H/Hz	τ	W_H/Hz	τ	W_H/Hz	Me_3C
(VIIIa)	5·15	8 *eq*	5·47	8 *eq*			9·18
(VIIIb)			5·20	8 *eq*	6·05	7 *eq*	9·12
(VIIIc)					6·05 *	7·5 *eq*	9·13
(VIIId)	5·24	8 *eq*	5·32	8 *eq*			9·20
(VIIIe)			5·1 *	7·5 *eq*			9·12
(VIIIf)			5·29	7·5 *eq*	5·91	8·0 *eq*	9·12
(VIIIg)	5·38	8 *eq*			6·18	8·0 *eq*	9·17
(VIIIh)	5·55	8 *eq*			6·05	7·0 *eq*	9·25
(XIa)			4·8	5 *eq*	6·27	11 *ax*	9·18
(XIb)			5·23	12 *ax*	5·87	5 *eq*	9·11
(XIc)			{4·65	7 *eq*			9·16
			5·15	12 *ax*			
(XIIa)			4·9	5·5 *eq*	6·3	10 *ax*	9·12
(XIIb)			5·2	11 *ax*	6·0	3·5 *eq*	9·12
(XIIc)			{5·2	13 *ax*			9·16
			4·7	5·5 *eq*			
(XIId)					6·2 *	7·5 *eq*	9·13

* Overlapping signals for two protons.

appeared in the range τ 4·7—5·4 and those α to the hydroxy-group in the range τ 5·9—6·4. The W_H value

[7] J. Sicher, F. Sipos, and M. Tichy, *Coll. Czech. Chem. Comm.*, 1961, **26**, 847.
[8] S. Winstein and H. Holness, *J. Amer. Chem. Soc.*, 1955, **77**, 5562.

of the signals for the axial protons is wider than those for the equatorial protons [9] and the signal for the equatorial protons resonates 0·5—0·3 p.p.m. downfield from the corresponding axial protons.[10]

In the 5α-cholestane series the 2α-alcohol (Va) was the only diacetate isolated when the ether (IV) was treated with boron trifluoride followed by ice; [4] however, when the ether (IV) was treated with boron trifluoride in acetic anhydride and then refluxed with water for 4 h, a mixture, separable by preparative t.l.c., of the two diacetates (Va and b) was obtained in the ratio 3 : 1 as determined by the n.m.r. integral of the 2β-H and 3β-H respectively. G.l.c. analysis gave a single peak with retention time corresponding to the ether (IV) suggesting thermal regeneration of the ether (IV) as observed on attempted g.l.c. analysis of similar compounds without the 3α-acetoxy-group.[4,11]

Stereoselectivity involving the hydrolysis of acetoxonium ions has been observed [12] on hydrolysis of suitably orientated α-epoxy-acetates. Cholest-4-en-3β-yl acetate gave a mixture of α- and β-epoxides (XIII) and (XIV) with peracid.[11] The former has the 3β-acetoxy-group in a suitable steric environment for participation to give the acetoxonium ion (XV), and treatment with sulphuric acid in acetone followed by cold water gave the 4β-monoacetate (XVIa). Under the same conditions the β-epoxide (XIV) gave only the 3β-acetate (XVIb) expected by S_N2 attack at C-5 by water or by opening of the protonated epoxide to give a C-5 carbonium ion followed by attack of water from the less hindered side. These results are similar to those obtained by Julia and Furer [12] in the androstane series. Refluxing the 4β-monoacetate (XVIa) in acetic anhydride yielded a mixture of the 4β-mono- (XVIa), the 3β-mono- (XVIb), and some 3β,4β-di-acetate (XVIc). The structure assignments were made on the basis of n.m.r. analysis and the relative data are shown in Table 2.

TABLE 2

N.m.r. data in the steroid series

	Protons α to acetoxy		Protons α to hydroxy		19-Methylene		OAc
Compd.	τ	W_H/Hz	τ	W_H/Hz	τ	J_{AB}	τ
(Va)	4·82	6·5	6·18	21	5·70	12	
					5·92		
(Vb)	5·13	21	5·93	6·5	5·78	A_2	
(XVIa)	5·07	J_4	5·73	25			7·92
(XVIb)	4·76	25	6·36	J_4			7·87
(XVIc)	4·60	25					8·0, 7·86
	4·97	J_4					

These results show the generality of the hydrolysis of acetoxonium ions at low temperature (kinetic control) to give *cis*-hydroxy-acetates in which the hydroxy-group is almost exclusively equatorial. King and Allbutt [3] have suggested that this may be due to a combination of steric and stereoelectronic effects. Under thermodynamic conditions an equilibrium mixture of the two hydroxy-acetates is obtained.

[9] A. Hassner and C. Heathcock, *J. Org. Chem.*, 1964, **29**, 1350.
[10] E. L. Eliel and M. H. Gianni, *Tetrahedron Letters*, 1962, 97.

EXPERIMENTAL

M.p.s were determined with a Köfler hot stage apparatus. I.r. spectra (in carbon tetrachloride) were measured with a Perkin-Elmer 221 spectrophotometer. N.m.r. spectra were measured with Varian A60 or HA100 instruments with deuteriochloroform as solvent and tetramethylsilane as internal reference. Mass spectra were measured with an MS9 double-focusing mass spectrometer. Column chromatography was performed on alumina, deactivated by washing with 2N-acetic acid, or silica (Davison, 100—200 mesh). T.l.c. was carried out on silica plates in benzene and the plates were visualised by spraying with conc. sulphuric acid and heating. Preparative t.l.c. was carried out on silica plates in ether–hexane (1 : 4); the plates were sprayed with berberine hydrochloride and examined in u.v. light. G.l.c. was performed in an F and M 400 instrument fitted with a disc integrator on a column (1·75 m × 3 mm) packed with 1% silicone rubber (nitrile) XE60 on acid-washed silanised Gas Chrom P (100—140 mesh), or on a column (1·1 m × 3 mm) packed with 3·8% SE30 on Diatoport S (80—100 mesh), the injection port and detector were *ca.* 60° higher than the column temperature, and helium was used as the carrier gas at a flow rate of 75 ml min^{-1}. Microanalyses were performed by the Australian Microanalytical Service, Melbourne. Light petroleum refers to a fraction, b.p. 55—65°.

Acetoxy-tosylate (VIIIa).—*trans*-1,2-Epoxy-4-t-butylcyclohexane [5,6] (2·3 g) was treated with acetic anhydride (7·5 g) in toluene-*p*-sulphonic acid monohydrate (3·3 g) below 40° for 3 h. The mixture was poured into ice–water (50 ml) and the crude product was purified by preparative t.l.c. on silica gel with ether–benzene (1 : 3) to give t-2-*acetoxy*-c-4-t-*butylcyclohexyl* r-*tosylate* (VIIIa) (2·1 g), m.p. 96—97° (Found: C, 62·3; H, 7·7; S, 8·5. $C_{19}H_{28}O_5S$ requires C, 62·1; H, 7·7; S, 8·7%), n.m.r. data in Table 1. Also isolated was r-1,t-2-*diacetoxy*-c-4-*t-butylcyclohexane* (VIIIe) (150 mg) (Found: C, 65·5; H, 9·3. $C_{14}H_{24}O_4$ requires C, 65·6; H, 9·4%), n.m.r. data in Table 1 and τ 7·93 (OAc).

Acetoxy-tosylate (VIIId).—4-t-Butylcyclohexene [7] (12 g) was added slowly to a solution of toluene-*p*-sulphonic acid monohydrate (20 g) and hydrogen peroxide (30%; 12 g) in acetic anhydride (45 g) keeping the temperature below 40°. After standing for 3 h at 20—25° the mixture was poured into water (200 ml) to give a yellow oil. The crude product was purified by preparative t.l.c. on silica gel in ether–benzene (1 : 5) to give a mixture of the acetoxy-tosylates (VIIIa and VIIId) (8·2 g), n.m.r. in Table 1. After standing for several h crystallisation took place and recrystallisation from methanol gave t-2-*acetoxy*-t-5-*t-butylcyclohexyl* r-*tosylate* (VIIId), m.p. 100—101° (Found: C, 62·2; H, 7·6. $C_{19}H_{28}O_5S$ requires C, 62·1; H, 7·7; S, 8·7%), n.m.r. data in Table 1. Also isolated by preparative t.l.c. were (i) the *trans*-diacetate (VIIIe) (1·5 g) identical with a sample prepared previously; (ii) a mixture of the hydroxy-tosylates (VIIIg) and (VIIIh) (60 mg), $\nu_{max.}$ 3450 (OH), 1740, and 1250 (tosylate) cm^{-1}, n.m.r. data in Table 1; and (iii) a mixture of the hydroxy-acetates (VIIIb) and (VIIIf) (980 mg) (Found: C, 67·3; H, 10·4. Calc. for $C_{12}H_{22}O_3$: C, 67·25; H, 10·35%), n.m.r. data in Table 1; and c-4-*t-butylcyclohexane*-r-1,t-2-*diol* (VIIIc) (56 mg)

[11] C. W. Shoppee, J. C. Coll, and R. E. Lack, *J. Chem. Soc.* (*C*), 1970, 1893.
[12] S. Julia and B. Furer, *Bull. Soc. chim. France*, 1966, 1106.

(Found: C, 69·9; H, 11·5. $C_{10}H_{20}O_2$ requires C, 69·8; H, 11·6%), n.m.r. data in Table 1.

Reactions of trans-*Acetoxy-tosylates* (VIIIa *and* VIIId).—(a) *Glacial acetic acid.* (i) The acetoxy-tosylate (VIIIa) (1 g) was heated under reflux with glacial acetic acid (10 ml) and potassium acetate (1 g) for 4 h. After cooling, the mixture was poured into ice–water and extracted with ether to give an oil (800 mg). This mixture was separated by preparative t.l.c. to give c-2-*hydroxy*-t-5-*t-butylcyclohexyl* r-*acetate* (XIa) as an oil (400 mg) (Found: C, 67·3; H, 10·4. $C_{12}H_{22}O_3$ requires C, 67·25; H, 10·35%), n.m.r. data in Table 1 and τ 7·95 (OAc). Also isolated was the *trans*-diacetate (VIIIe) as an oil (50 mg) identical with a sample previously prepared.

(ii) The acetoxy-tosylate (VIIIa) (1 g) was similarly treated to give c-2-*hydroxy*-c-4-*t-butylcyclohexyl* r-*acetate* (XIIa) as an oil (120 mg) (Found: C, 67·3; H, 10·35. $C_{12}H_{22}O_3$ requires C, 67·25; H, 10·35%), n.m.r. data in Table 1 and τ 8·6 (1H, OH, disappears on addition of D_2O), 7·88 (OAc). Also isolated was the *trans*-diacetate (VIIIe) identical with sample prepared previously.

(b) *Aqueous acetic acid.* (i) The acetoxy-tosylate (VIIIa) (1 g) was heated under reflux for 4 h with aqueous acetic acid (1 : 1) containing potassium acetate (1 g). After cooling, the mixture was poured into ice–water and extracted with ether to give an oil shown by t.l.c. to be a mixture of four compounds which were separated by preparative t.l.c. on silica gel with ether–benzene (1 : 4) to give r-1,c-2-*diacetoxy*-t-4-*t-butylcyclohexane* (XIc) as an oil (Found: C, 66·1; H, 9·3. $C_{14}H_{24}O_4$ requires C, 65·6; H, 9·4%), n.m.r. data in Table 1 and τ 7·95 (2 × OAc); the *cis*-hydroxy-acetate (XIa) identical with the sample prepared above; c-2-*hydroxy*-t-4-*t-butylcyclohexyl* r-*acetate* (XIb) as an oil (Found: C, 67·5; H, 10·2. $C_{12}H_{22}O_3$ requires C, 67·25; H, 10·35%), n.m.r. data in Table 1 and τ 7·98 (OAc). The ratio of *cis*-monoacetates (XIa) and (XIb) was 3 : 5 as obtained in several separations by preparative t.l.c. on silica gel.

(ii) The acetoxy-tosylate (VIIId) (1 g) was similarly treated to give r-1,c-2-*diacetoxy*-c-4-*t-butylcyclohexane* (XIIc) as an oil (80 mg) (Found: C, 65·7; H, 9·5. $C_{14}H_{24}O_4$ requires C, 65·6; H, 9·4%), n.m.r. data in Table 1 and τ 8·0 and 7·9 (2 × OAc); the *cis*-hydroxy-acetate (XIIa) (310 mg) identical with the sample prepared above; c-2-*hydroxy*-c-5-*t-butylcyclohexyl* r-*acetate* (XIIb) (400 mg) as an oil (Found: C, 67·6; H, 10·45. $C_{12}H_{22}O_3$ requires C, 67·25; H, 10·35%), n.m.r. data in Table 1 and τ 7·88 (OAc); and c-4-*t-butylcyclohexane*-r-1,c-2-*diol* (XIId) (50 mg) as an oil [Found: *M* (mass spectrometry) 172·1469. $C_{10}H_{20}O_2$ requires *M*, 172·1463], n.m.r. data in Table 1.

(c) *Acetic anhydride and potassium acetate.* The acetoxy-tosylates (200 mg) (VIIIa) and (VIIId) were each converted into the *trans*-diacetate (VIIIe) (55 mg), identical with an authentic sample, when treated with acetic anhydride (20 ml) and potassium acetate (100 mg) under reflux for 3·5 h.

Acetolytic Cleavage of the Ether (IV) *with Boron Trifluoride.*—(a) *Kinetic control.* The ether (IV) (500 mg) in acetic anhydride (50 ml) and ether (10 ml) was treated with boron trifluoride–ether (35 drops) for 2 h. The mixture was poured onto ice and extracted with ether to give, after chromatography, the diacetate (Va), m.p. 126—128° (lit.,[4] 126—127°) (from pentane), and triacetate (Vd), m.p. 128—130° (lit.,[4] 129—130°) (from acetone–methanol).

(b) *Thermodynamic control.* The ether (IV) (500 mg) in acetic anhydride (50 ml) and ether (10 ml) was treated as above with boron trifluoride–ether (35 drops). After 2 h water (25 ml) and dioxan (5 ml) were added slowly and the solution was refluxed for 4 h. After isolation, the crude product was separated by preparative t.l.c. (50% ether–hexane) to give (i) 19-acetoxy-2α,3α-dihydroxycholestane (Vc) (50 mg), m.p. 107—109° (from methanol) [Found: *M* (mass spectrometry), 462·3709. $C_{29}H_{50}O_4$ requires *M*, 462·3713], τ 7·6 (OAc), 7·65 (2H, OH, exchanges with D_2O), 6·26 (W_H 10 Hz, 2-H), and 6·02 (W_H 6 Hz, 3-H); (ii) the hydroxy-acetate (Va) (130 mg), m.p. and mixed m.p. 126—128° (from pentane) (lit.,[4] 126—127°), τ 6·18 (W_H 21 Hz, 2-H), 5·18 (W_H 6·5 Hz, 3-H); (iii) 2α,19-*diacetoxy*-3α-*hydroxycholestane* (Vb) (260 mg), m.p. 85—86° (from pentane) [Found: *M* (mass spectrometry), 504·3815. $C_{31}H_{52}O_5$ requires *M*, 504·3821], τ 5·93 (W_H 6·5 Hz, 3-H) and 5·13 (W_H 21 Hz, 2-H); and (iv) the triacetate (Vd) (30 mg), m.p. and mixed m.p.[4] 128—130° (from acetone–methanol).

3β-*Acetoxycholest*-4-*ene*.—Cholest-4-en-3β-ol,[13] m.p. 133—134°, was treated with acetic anhydride in pyridine to give 3β-acetoxycholest-4-ene, m.p. 84—86° (lit.,[4] 86°), τ 9·06 (13-Me), 8·90 (10-Me), 7·92 (3β-OAc), 4·7 (W_H 17 Hz, 3α-H), and 4·73 (W_H 3 Hz, 4-H).

Acid Cleavage of the α-Epoxide.—Treatment of the epoxide (XIII)[14] (400 mg) in acetone (100 ml) and water (5 ml) with 2N-sulphuric acid (2 ml) for 48 h at 20° gave the monoacetate (XVIa) (450 mg), m.p. 187—189° (from acetone–methanol) (lit.,[12] 187—189°) (Found: C, 75·0; H, 10·7. Calc. for $C_{29}H_{50}O_4$: C, 75·3; H, 10·9%), τ 7·91 (2β-OAc), 5·73 (W_H 25 Hz, 3α-H), and 5·07 (d, *J* 4 Hz, 4α-H).

Equilibration of 4β-*Acetoxy*-5α-*cholestane*-3β,5α-*diol* (XVIa).—The monoacetate (XVIa) in acetic anhydride (15 ml) and water (3 ml) was heated under reflux for 4 h. The crude product was separated by preparative t.l.c. to give (i) the starting diol (XVIa) (20 mg); (ii) 3β-acetoxy-5α-cholestane-4β,5α-diol (XVIb) (20 mg), m.p. 196—198° (lit.,[12] 188—193°; lit.,[15] 196—199°) (Found: C, 75·4; H, 11·0. Calc. for $C_{29}H_{50}O_4$: C, 75·3; H, 10·9%), τ 9·07 (13-Me), 8·78 (10-Me), 7·87 (3β-OAc), 6·37 (d, *J* 4 Hz, 4α-H), and 4·76 (W_H 25 Hz, 3α-H); and (iii) the diacetate (XVIc) (15 mg), m.p. 139—140° (from methanol) (lit.,[16] 135°), τ 9·09 (13-Me), 8·84 (10-Me), 8·0 and 7·86 (3β- and 4β-OAc), 4·97 (d, *J* 4 Hz, 4α-H), and 4·60 (W_H 25 Hz, 3α-H).

One of us (A. M. S.) acknowledges the award of a University of Sydney Postgraduate Studentship. This work was supported by the Australian Research Grants Committee.

[1/2426 *Received, 17th December, 1971*]

[13] C. W. Shoppee, J. K. Hummer, R. E. Lack, P. Ram, and S. K. Roy, *Tetrahedron*, 1966, 315.
[14] D. J. Collins, *J. Chem. Soc.*, 1959, 3919.
[15] L. F. Fieser, T. Goto, and B. Bhattacharyja, *J. Amer. Chem. Soc.*, 1960, **82**, 7100.
[16] S. Julia and J. P. Lavaux, *Bull. Soc. chim. France*, 1963, 1238.