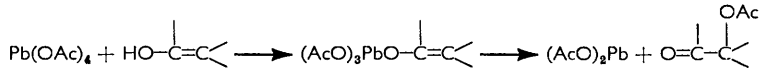
881. *Reactions of Ketones with Oxidising Agents. Part I. Catalysis of the Ketone–Lead Tetra-acetate Reaction with Boron Trifluoride.*

By H. B. Henbest, D. N. Jones, and G. P. Slater.

Ketones are acetoxylated by lead tetra-acetate at room temperatures when boron trifluoride is present as catalyst, cholestan-2- and -3-one giving the 3α-acetoxy- (VII) and 2α-acetoxy-ketone (II), respectively. 2α-Acetoxycholestan-3-one isomerises on alumina to 3β-acetoxycholestan-2-one (III); and the fourth ketol acetate of this group, 2β-acetoxycholestan-3-one (IX), has been prepared by oxidation of 2β-acetoxycholestan-3α-ol. The ultraviolet absorption of 2β-acetoxycholestan-3-one is unusual, the axial acetoxy-group giving a small hypsochromic shift. The rotatory dispersions of the four acetoxy-ketones are briefly discussed, the most striking feature being the reduced amplitude caused by introduction of an axial acetate group.

One of the reactions of lead tetra-acetate with organic compounds is to introduce an acetoxy-group into a position adjacent to a carbonyl group.[1] Kinetic [2] and other evidence suggests that enolisation of the carbonyl compound can be the first, and largely rate-determining, step of the reaction. In view of the evidence that alcohols react with lead tetra-acetate to give alkoxylead triacetates,[3,4] the enolic form of the carbonyl compound probably gives an ester that decomposes to lead diacetate with intramolecular donation of an acetoxy-group to the adjacent carbon atom:

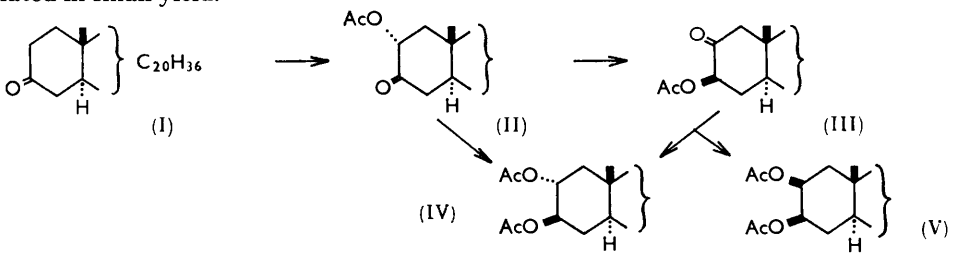


[1] Dimroth and Schweizer, *Ber.*, 1923, **56**, 1375.
[2] Iohikana and Yamakuchi, *J. Chem. Soc. Japan*, 1952, **73**, 415; *Chem. Abs.*, 1953, **47**, 10,474.
[3] Cordner and Pausacker, *J.*, 1953, 102.
[4] Henbest. *Ann. Reports*, 1956, **53**, 146.

If the carbonyl compound is appreciably enolised (*e.g.*, for β-diketones), reaction with lead tetra-acetate often occurs readily at 10—40°,[1,5,6] although by-products arising from dehydrogenative coupling of the carbonyl compound and indicative, therefore, of a competing radical reaction are sometimes obtained.[5,7] Phenols, like enols, react readily with lead tetra-acetate and *o*- and *p*-acetoxy-compounds are formed;[8] the mechanism is probably similar to that of the enol reaction although the route by which the acetate group reaches the *para*-position requires clarification. The easily enolised βγ-unsaturated ketone, cholest-5-en-3-one, reacts with lead tetra-acetate at 15—20°, giving the 4α-acetoxy-compound.[9] Higher temperatures (70—100°) are required for acetoxylation of 3-oxo-Δ^4-steroids and most saturated ketones at convenient rates.[10,11] As radical and other species are formed when lead tetra-acetate is heated to 70° and above,[12] use of the normal reaction conditions for acetoxylating saturated ketones could result in side reactions, especially if other functional groups, reactive towards radicals, are present. Lower temperatures could probably be used if enolisation could be accelerated, and this led to our trying boron trifluoride as catalyst. This reagent is effective for the acylation of ketones by acid anhydrides,[13] reactions that presumably also involve initial enolisation of the carbonyl compound. Use of many of the usual acidic and basic catalysts is ruled out by their reactions with the quadrivalent lead salt.

Reaction between cholestan-3-one (I) and lead tetra-acetate (1·1 mol.) occurred at 25° if boron trifluoride was added (its ether complex was used). Rates of reaction were similar in ether and acetic acid but greater in benzene. Addition of isopropyl alcohol to the benzene solution slowed the reaction. Oxygen-containing solvents no doubt compete with cholestanone for the boron trifluoride (cf. a similar difference between ether and benzene in the boron trifluoride-catalysed isomerisation of a 9α,11α-epoxy-Δ^7-steroid [14]). In contrast, acetoxylation of cyclohexanone at 80° in the absence of a catalyst is faster in acetic acid than in benzene,[5] the former solvent assisting enolisation.

Chromatography of the product from cholestanone on deactivated alumina (see below) gave the new 2α-acetoxycholestanone (II) as the only isolable acetoxy-ketone; the best yields (50%) were obtained by using benzene or benzene–isopropyl alcohol as reaction solvent. Reactions in ether or acetic acid gave the same acetoxy-ketone, but in the latter solvent some αβ-unsaturated ketone was always formed, and cholest-1-en-3-one was isolated in small yield.

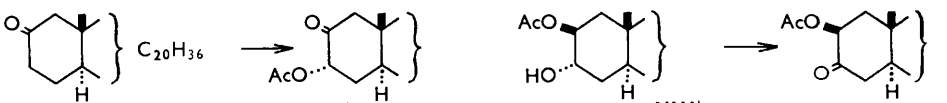


The structure (II) for the acetoxylation product was established by reduction with lithium aluminium hydride: cholestane-2α,3β-diol [15] was the main product [isolated as the

[5] Cavill and Solomon, *J.*, 1955, 4426.
[6] Fuson, Maynert, Tan, Trumbull, and Wassmundt, *J. Amer. Chem. Soc.*, 1957, **79**, 1938.
[7] Cocker and Schwarz, *Chem. and Ind.*, 1951, 390.
[8] Wesseley, Kotlan, and Metlesics, *Monatsh.*, 1954, **85**, 69; Hecker, *Chem. Ber.*, 1959, **92**, 1386; Gold and Schwenk, *J. Amer. Chem. Soc.*, 1958, **80**, 5683.
[9] Fieser and Stevenson, *J. Amer. Chem. Soc.*, 1954, **76**, 1728.
[10] Seebeck and Reichstein, *Helv. Chim. Acta*, 1944, **27**, 948.
[11] Fieser and Romero, *J. Amer. Chem. Soc.*, 1953, **75**, 4716.
[12] Benson, Sutcliffe, and Walkley, *J. Amer. Chem. Soc.*, 1959, **81**, 4488.
[13] Meerwein, *Ber.*, 1933, **66**, 411; Meerwein and Vossen, *J. prakt. Chem.*, 1934, **141**, 149.
[14] Bladon, Henbest, Jones, Lovell, Wood, Woods, Elks, Evans, Hathway, Oughton, and Thomas, *J.*, 1953, 2921.
[15] Henbest and Smith, *J.*, 1957, 926; Shoppee, Jones, and Summers, *J.*, 1957, 3100.

diacetate (IV)] and cholestane-2α,3α-diol was also formed. Adsorption on active alumina converted the acetoxy-ketone (II) into the isomer (III); the isomerisation proceeds by enolisation and acyl group migration *via* a cyclic intermediate (cf. the isomerisation of 4α-acetoxycholest-5-en-3-one on alumina [9]). Reduction of compound (III) with lithium aluminium hydride gave cholestane-2α,3β- and -2β,3β-diol, isolated as diacetates (IV) and (V). 3β-Acetoxycholestan-2-one has been obtained before,[16] by acyloin condensation of a 2,3-seco-diester and acetylation of the resultant ketol mixture. Identity of physical properties and a mixed m. p. determination with a sample provided by Professor J. C. Sheehan confirmed that the products from the two routes were identical. 2α-Acetoxycholestan-3-one has not been described before, the product formed in the reaction of 2α-bromocholestan-3-one with sodium acetate [17] having been shown by indirect evidence [11] to be an inseparable mixture of 2α- and 4α-acetoxycholestanone; a minor product from the acyloin reaction, tentatively regarded [16] as 2α-acetoxycholestanone, was clearly different from the pure compound derived from the acetoxylation reaction.

Our structural assignments were further confirmed by the preparation and properties of the two remaining isomers containing acetate and carbonyl groups at positions 2 and 3. The boron trifluoride-catalysed reaction of cholestan-2-one (VI) with lead tetra-acetate in acetic acid gave an acetoxy-ketone, different from compound (III), and therefore considered to be 3α-acetoxycholestan-2-one (VII) (enolisation towards $C_{(3)}$, not $C_{(1)}$, is preferred for



energy reasons [18,19]). In agreement with structure (VII), a bathochromic shift [140 Å relative to the value for (VI)] was observed in the ultraviolet absorption peak. The remaining isomer, 2β-acetoxycholestan-3-one (IX), was obtained by oxidation of the acetoxy-alcohol (VIII) obtained [20] by acetolysis of 2α,3α-epoxycholestane. It was rapidly isomerised, even on deactivated alumina, to the 2α-acetoxy-compound (II) in which the substituent is equatorial (cf. the similar isomerisation of 2β- to 2α-bromocholestanone [21]).

Each of the four acetoxy-ketones was treated with lead tetra-acetate in acetic acid in the presence of boron trifluoride, the conditions used for acetoxylation of the unsubstituted ketones. 3α- and 3β-Acetoxycholestan-2-one were recovered in 70 and 90% yield, respectively, and there is therefore little doubt that the former compound is the primary reaction product from acetoxylation of cholestan-2-one. Under the same conditions, 2α-acetoxycholestanone was partly recovered (45%) and partly converted into unsaturated ketone. 2β-Acetoxycholestanone was converted in considerable part into material containing more oxygen. Although the presence of some 2α-acetoxycholestanone in this material cannot be excluded, the fact that the 2α-acetoxy-compound is not a major product from the 2β-acetoxy-compound under acetoxylation conditions strongly indicates that the latter compound is not an intermediate in the formation of the 2α-acetoxy-compound from the 3-ketone. The experiments, as a whole, suggest that acetoxylation parallels the bromination of the 2- [19] and 3-ketones, α-attack predominating for steric reasons.

The acetoxylation of cholestan-3-one is also promoted by perchloric acid, the reaction in acetic acid at 25° giving 2α-acetoxycholestanone (14% on non-recovered cholestanone) and unchanged ketone (22%); this method is therefore inferior from the preparative

[16] Sheehan and Erman, *J. Amer. Chem. Soc.*, 1957, **79**, 6050.
[17] Ruzicka, Plattner, and Aeschbacher, *Helv. Chim. Acta*, 1938, **21**, 866.
[18] Henbest, Meakins, and Wood, *J.*, 1954, 800.
[19] Djerassi and Nakano, *Chem. and Ind.*, 1960, 1385.
[20] Fürst and Plattner, *Helv. Chim. Acta*, 1949, **32**, 275.
[21] Alt and Barton, *J.*, 1954, 4284.

point of view. Hydrogen fluoride, which might be formed in traces in the reactions in which boron trifluoride was used as catalyst, was less effective, only a trace of acetoxy-ketone being formed; this is probably due to the conversion of the lead tetra-acetate into lead tetrafluoride.

Rotatory Dispersion and Ultraviolet Absorption of Acetoxy-ketones.—The 3α- and 3β-acetate groups in compounds (VII) and (III) are relatively unhindered and should be particularly suitable for the determination of the effects of axial and equatorial acetoxy-groups on the rotatory dispersion and ultraviolet absorption properties of the 3-ketone group. The 2α-equatorial acetate in compound (II) is also unhindered, but steric overlap of the axial 2β- and 10β-substituents in the acetoxy-ketone (IX) may cause it to show abnormal absorption and rotation properties. Previous work on steroid acetoxy-ketones has been carried out with compounds substituted in ring B, C, or D, where special steric or conformational factors could affect the situation.

Equatorial acetates. Small hypsochromic shifts in the ultraviolet spectrum have been recorded before [22] for steroid ketones with equatorial acetoxy-substituents. The acetate groups in compounds (III) and (II) gave small bathochromic and hypsochromic effects, respectively. They also only caused small changes in the Cotton curves of the ketones.

Axial acetates. In the ultraviolet spectrum, the 3α-acetate group (in VII) gave a bathochromic shift of 14 mμ, compared with shifts of 25 and 32 mμ given, respectively, by chlorine and bromine.[22] The absorption of the other axial acetoxy-ketone (IX) was unusual in giving a small hypsochromic effect, although it may be noted that an axial chlorine in this position shows [22] a smaller bathochromic shift (14 mμ) than usual. Both results suggest that the ring is forced out of the normal chair conformation by overlapping of the 2β- and 10β-axial substituents.

Axial halogen substituents cause the first peak of the rotatory dispersion spectrum to shift by 20—25 mμ to longer wavelengths.[23] Corresponding shifts given by the acetate groups in compounds (VII) and (IX) were 8 mμ and 1 mμ, the latter compound again showing atypical properties. Substitution of (axial) 3α- and 2β-bromine into 2- and 3-ketones, respectively, strongly enhances the positive Cotton curves of the parent ketones, whereas the corresponding acetates (VII) and (IX) gave curves with considerably reduced amplitudes.[24]

Boron trifluoride-catalysed acetoxylations of other oxo-steroids will be reported later.

Experimental

M. p.s were determined on a Kofler block. Rotations were determined for chloroform solutions. Light petroleum refers to the fraction of b. p. 30—40°. Alumina refers to Spence (type H); when necessary, it was deactivated with 5% of 10% acetic acid. Solvents used for reactions were purified by standard methods.

Acetoxylation of Cholestan-3-one (I).—A solution of the ketone (5 g., 1 mol.) and lead tetra-acetate (6·34 g., 1·1 mol.) in acetic acid (222 ml., 300 mol.) containing boron trifluoride–ether complex (9·6 ml., 5·85 mol.) was stirred at 25° under nitrogen. After 145 min. the starch–iodide test for lead tetra-acetate was negative. Isolation with ether gave a yellow oil (5·62 g.) that became semi-solid; its infrared spectrum indicated the presence of acetate and unsaturated ketone groups. It was dissolved in pentane and adsorbed on to Florisil (170 g.). Elution with pentane gave cholestanone, followed by mixtures of this compound with unsaturated ketone (see below). Elution with pentane–benzene (9 : 1) gave *2α-acetoxycholestan-3-one* (II) (2·95 g., 51% based on initial cholestanone), m. p. 123—125° (from acetone–ethanol), $[\alpha]_D$ +57° (Found: C, 78·45; H, 10·75. $C_{29}H_{48}O_3$ requires C, 78·3; H, 10·9%). The fractions containing unsaturated ketone were combined (0·75 g.) and adsorbed on to alumina (75 g.). Elution with pentane–benzene (3 : 1) gave cholestanone (total recovery, 190 mg.). Elution

[22] Cookson, *J.*, 1954, 282; Cookson and Dandegaonker, *J.*, 1955, 352.
[23] Djerassi, "Optical Rotatory Dispersion," McGraw-Hill, New York, 1960, pp. 118—121.
[24] Amplitude defined by Djerassi and Klyne, *Proc. Chem. Soc.*, 1957, 55.

with pentane–benzene (2 : 1) gave material (402 mg.) ($\lambda_{max.}$ 2350 Å in EtOH) from which cholest-1-en-3-one (100 mg.), m. p. and mixed m. p. 96—98°, was obtained by crystallisation from acetone–ethanol.

αβ-Unsaturated ketone was formed in appreciable amounts only in the reactions in acetic acid. The normal reaction time (to give a negative starch–iodide test) in acetic acid (140—150 min.) was increased to 260 and 400 min. by the presence of 0·33 mol. % of isopropyl alcohol and water, respectively; *ca.* 9% of unsaturated ketone was formed in both of these reactions (*ca.* 10% formed in pure acetic acid). These percentages are calculated by using the molecular extinction (ε 10,700) of cholest-1-en-3-one; the absorption peak (near 2350 Å) of the total unsaturated ketonic product suggests that another compound, possibly cholest-4-en-3-one, is present.

Not all of the lead tetra-acetate dissolved when it was added to the ketone in acetic acid, but the addition of catalyst gave a clear solution.

A mixed m. p. of 2α-acetoxycholestan-3-one with a compound (m. p. 147—149°) tentatively regarded [16] as having this structure gave a value of 121—126°, 137—145° (double m. p.). There was no doubt that the compounds were different.

The reaction between cholestanone (500 mg.) and lead tetra-acetate (1·1 mol) was carried out at 25° in various solvents containing boron trifluoride–ether complex (5·85 mol.). The annexed Table gives the times for complete reaction of the tetra-acetate and the yields of cholestanone and 2α-acetoxycholestanone, determined by chromatographic separation on deactivated alumina, the compounds being eluted respectively with light petroleum and light petroleum–benzene (4 : 1). Use of more active alumina caused the formation of some 3β-acetoxycholestan-2-one (see below).

Solvent (mol.)	Reaction time (min.)	Cholestanone recovered (%)	2α-Acetoxy-cholestanone (%) *
Ether (300)	155	20	36
Benzene (300) + isopropyl alcohol (10) ...	230	14	51
Benzene (300)	47	6	51

* These yields are based on the cholestanone not recovered from the reaction.

Addition of the tetra-acetate to the ketone in dry benzene gave a brown suspension which became a clear solution when the boron trifluoride–ether complex was added.

When 1·5 mol. of lead tetra-acetate was used for the reaction in benzene, the reaction time was 330 min. and 2α-acetoxycholestanone (51%) but no cholestanone was obtained.

The experiment using lead tetra-acetate (1·1 mol.) and benzene as solvent was repeated without the addition of boron trifluoride. After 47 min. the mixture was processed, to give cholestanone (92% recovery). The infrared spectrum of the total crude product gave no indication of the presence of acetoxy-ketone or unsaturated ketone.

Experiments with other catalysts. (*a*) Perchloric acid * (5 mol.) was added to a solution of cholestanone (500 mg., 1 mol.) and lead tetra-acetate (1·1 mol.) in acetic acid (300 mol.) at 25°. The tetra-acetate had reacted after 10 min. Chromatography of the neutral product (538 mg.) gave cholestanone (112 mg., 22%) and 2α-acetoxycholestanone (60 mg., 14% based on unrecovered cholestanone). The alkaline washings from the isolation procedure were acidified and extracted with ether, to give a brown solid (30 mg.). Crystallisation from acetone and from ethyl acetate gave 2,3-seco-5α-cholestane-2,3-dioic acid, m. p. and mixed m. p. 195—196°.

The infrared and ultraviolet absorption of the crude neutral product showed that αβ-unsaturated ketone was absent. Using the longer reaction time of 55 min. led to *ca.* 12% of unsaturated ketone.

(*b*) Cholestanone (500 mg., 1 mol.) and lead tetra-acetate (1·1 mol.) in acetic acid (300 mol.) containing hydrogen fluoride (11 mol.) were stirred at 25° in a Polythene container. After 6·5 hr. the tetra-acetate had not completely dissolved and more acetic acid (256 mol.) and hydrogen fluoride (11 mol.) were added. After 26·5 hr. the test for lead tetra-acetate was still positive, and the product (533 mg.) was isolated as usual. The infrared spectrum showed that a small amount of acetoxy-ketone was present, but chromatography on deactivated alumina (16 g.) gave cholestanone (170 mg.) as the only solid product.

Acetoxylation of Cholestan-2-one (VI).—Boron trifluoride–ether complex (0·66 ml., 5 mol.)

* Perchloric acid (67% in water) was used; it was dehydrated with the calculated amount of acetic anhydride and the acetic acid formed constituted part of the final 300 mol.

was added to cholestan-2-one (400 mg., 1 mol.) in acetic acid (17·78 ml., 300 mol.) at 25°. After 6 hr. more catalyst (0·88 ml., 6·7 mol.) was added; the test for tetra-acetate then became negative after a further hour. Isolation with ether gave a yellow oil (460 mg.) that was dissolved in light petroleum (b. p. 40—60°) (20 ml.). 3α-*Acetoxycholestan-2-one* (VII) (107 mg.), m. p. 145—148°, separated when the solution was kept. The pure acetoxy-ketone had m. p. 148—149° (from acetone–ethanol), $[\alpha]_D$ +57° (Found: C, 78·5; H, 10·7%). Chromatography of the remainder of the product on deactivated alumina (22·5 g.) gave oils (elution with light petroleum) and more 3α-acetoxycholestan-2-one (80 mg.; total yield 40%), m. p. 146—148°.

2β-*Acetoxycholestan-3-one* (IX).—Oxidation of 2β-acetoxycholestan-3α-ol (VIII) (400 mg.; m. p. 115—117°; lit.,[20] m. p. 113°) by the chromic acid in acetone method [25] gave 2β-*acetoxycholestan-3-one* (288 mg., 73%), m. p. 144—146° (from acetone–methanol), $[\alpha]_D$ +94° (Found: C, 78·15; H, 11·05%). The m. p. was depressed to *ca.* 120° on admixture with either 3α- or 3β-acetoxycholestan-2-one.

Acetylation of 2β-acetoxycholestan-3α-ol with pyridine–acetic anhydride gave 2β,3α-diacetoxycholestane, m. p. 141—142° (from acetone–methanol), $[\alpha]_D$ +60° (Found: C, 76·25; H, 10·5. Calc. for $C_{31}H_{52}O_4$: C, 76·2; H, 10·7%). The mixed m. p. with an authentic sample (m. p. 137—138°) was 138—140°.

Light absorption and rotatory dispersion of the acetoxy-ketones.

Acetoxy-ketone	Infrared C=O absorption (cm.$^{-1}$)	Ultraviolet absorption $\lambda_{max.}$ (Å) (log ε)	Rotatory dispersion [ϕ] peak (Å), [ϕ] trough (Å)	amplitude ($10^{-2}a$)
(II)	1759, 1740	2800 (1·56)	+3060 (3100) −3560 (2700)	+66
(IX)	1758, 1743	2820 (1·39)	+4370 (3080) −148 (2630)	+45
(III)	1756, 1735	2850 (1·53)	+7300 (3080) −4300 (2680)	+116
(VII)	1756, 1730	2940 (1·62)	+3400 (3180) −1740 (2780)	+52

Infrared spectra were determined for carbon tetrachloride, ultraviolet spectra for ethanol, and rotatory dispersions for methanol solutions.

The Action of Lead Tetra-acetate on the Acetoxy-ketones.—2α-*Acetoxycholestan-3-one.* The acetoxy-ketone (100 mg.) and lead tetra-acetate (127 mg., 1·3 mol.) in acetic acid (4·45 ml., 350 mol.) containing boron trifluoride–ether complex (0·19 ml., 6·8 mol.) were stirred under nitrogen at 25° for 1 hr., the test for lead tetra-acetate remaining strongly positive. Isolation gave a brown oil (94 mg.), containing an αβ-unsaturated ketone (infrared evidence). Crystallisation from acetone gave 2α-acetoxycholestan-3-one, m. p. 121—123° (45 mg., 45% recovery). The ultraviolet spectrum of the mother liquor indicated that cholest-1-en-3-one (8%) had been formed.

3α- and 3β-Acetoxycholestan-2-one were recovered in 89% and 70% yield, respectively, after similar treatment for 1·5 and 2 hr., respectively.

2β-*Acetoxycholestan-3-one.* This was similarly treated with lead tetra-acetate whereupon a compound, m. p. 154—156°, was formed. The constitution of this compound will be discussed in a later paper.

Reactions on Alumina.—2β-*Acetoxycholestan-3-one.* The acetoxy-ketone (210 mg.), dissolved in pentane–benzene (9 : 1), was adsorbed on deactivated alumina (6·4 g.) for 1 hr. Elution with pentane–benzene (9 : 1) gave 2α-acetoxycholestan-3-one (148 mg., 71%), m. p. and mixed m. p. 123—124°.

2β-Acetoxycholestan-3-one (250 mg.) in pentane–benzene (9 : 1) was placed on a column of active alumina (7·5 g.) and similar elution was commenced immediately: 2α-acetoxycholestan-3-one (163 mg., 65%), m. p. and mixed m. p. 123—125°, but no 3β-acetoxycholestan-2-one, was obtained.

2α-*Acetoxycholestan-3-one.* The acetoxy-ketone (150 mg.) in benzene was adsorbed on active alumina (10 g.) for 16 hr. Elution with benzene gave 3β-acetoxycholestan-2-one, m. p. 146—147° (30 mg., 20%), $[\alpha]_D$ +76° (Found: C, 78·8; H, 10·9%), followed by starting material,

[25] Bowden, Heilbron, Jones, and Weedon, *J.*, 1946, 39.

m. p. 122—129° (67 mg., 45% recovery). A sample (m. p. 138—141°) of 3β-acetoxycholestan-2-one supplied by Professor J. C. Sheehan gave, on admixture with our sample, a m. p. of 141—145°. The mixed m. p. with our sample of 3α-acetoxycholestan-2-one (m. p. 148—149°) gave a depression to 116—130°.

Reduction of 3β-Acetoxycholestan-2-one (III).—The acetoxy-ketone (250 mg.) was reduced with lithium aluminium hydride (100 mg.) in boiling ether (25 ml.) for 20 min. The product was treated with acetic anhydride and pyridine at 20° overnight, and the acetate was chromatographed on deactivated alumina (22 g.). Elution with light petroleum gave 2α,3β-diacetoxycholestane (IV) (30 mg.), m. p. and mixed m. p. 112—113° (from methanol), whilst elution with light petroleum–benzene (19 : 1) gave 2β,3β-diacetoxycholestane (V) (47 mg.), m. p. and mixed m. p. 123—125° (from methanol). These compounds also showed infrared spectra identical with those of authentic samples. Further elution with light petroleum–benzene gave a compound (15 mg.), m. p. 156—158°, which displayed an infrared spectrum consistent with that of an acetoxy-alcohol.

Reduction of 2α-Acetoxycholestan-3-one (II).—This compound (250 mg.) was reduced as in the previous experiment. Acetylation and chromatography on deactivated alumina (14 g.) gave 2α,3β-diacetoxycholestane (IV) [151 mg.; eluted with pentane–benzene (19 : 1)], m. p. and mixed m. p. 112—114°, and 2α,3α-diacetoxycholestane [22 mg.; eluted with pentane–benzene (3 : 1)], m. p. and mixed m. p. 134—136°.

We thank Glaxo Laboratories Ltd. for financial assistance (to G. P. S.), Professor J. C. Sheehan and Dr. G. H. R. Summers for samples, and Professor W. Klyne for rotatory dispersion measurements.

THE QUEEN'S UNIVERSITY OF BELFAST. [*Received, April 20th,* 1961.]