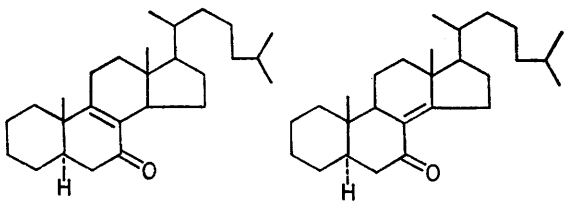
Mass Spectrometry in Structural and Stereochemical Problems. Part CCXX.[1] Synthesis and Mass Spectra of 5α-Cholest-8(9)- and 8(14)-en-7-ones

By **Ian Midgley** and **Carl Djerassi,*** Department of Chemistry, Stanford University, Stanford, California 94305, U.S.A.

5α-Cholest-8(14)-en-7-one (II) was prepared by a route known to produce authentic steroidal $\Delta^{8(14)}$-7-ketones, and the $\Delta^{8(9)}$-7-ketone (I) was obtained from a side product of this reaction. On the basis of chemical and spectroscopic evidence, it was shown that these samples are correctly formulated, whereas those reported earlier, by others, are not. Each of these enones undergoes a characteristic reaction in the mass spectrometer, and mechanisms for both diagnostically important processes are suggested.

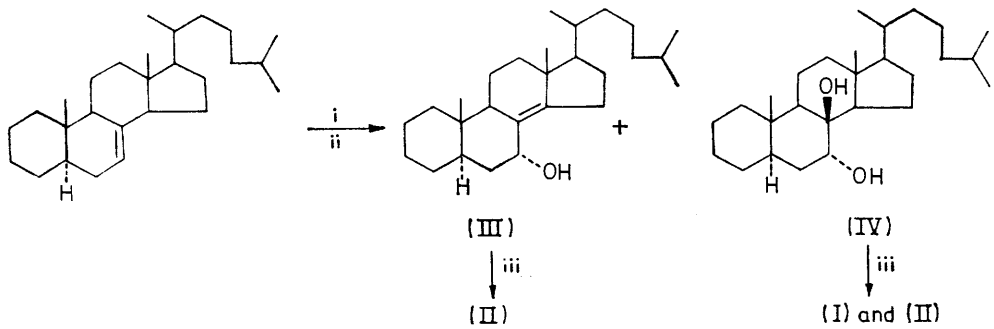
We recently had cause to prepare the little known Δ^{8}-7-ketones (I) and (II) as intermediates in the synthesis of



(I) (II)

certain deuterium-labelled steroidal olefins. In a recent communication,[2] Meakins *et al.* described the preparation of both enones (I) and (II) by the route depicted in Scheme 1, and the properties of the $\Delta^{8(9)}$-enone thus obtained were in reasonable agreement with those given in the only other available report of the synthesis of compound (I),[3] whereas the $\Delta^{8(14)}$-enone was apparently unknown prior to this.

Upon repeating these reactions, we indeed isolated two compounds whose m.p.s and optical rotations were similar to those given [2] for the supposed intermediates (III) and (IV), but the molecular weight of each, as determined by mass spectrometry, was 402, which corresponds not to a cholestanediol or cholestenol, but to a cholestenediol. Consistent with this formulation is our observation that oxidation of either product with Sarett's reagent [4] yields 5α-cholest-8(9)-ene-7,11-dione, so these enediols must be two of the four possible 5α-cholest-8(9)-ene-7,11-diols. The configurations of the hydroxy-groups in these two isomers can be deduced with a high degree of certainty from their n.m.r. spectra. Thus, in the spectrum of one enediol, the two >C*H*–OH protons absorb at δ 4·04 ($W_{\frac{1}{2}}$ *ca.* 6 Hz) and 4·47 p.p.m. ($W_{\frac{1}{2}}$ *ca.* 14 Hz); in the spectrum of the other isomer, the latter signal is identical in all respects, but the former occurs at δ 4·07 and has $W_{\frac{1}{2}}$ *ca.* 12 Hz. Since such protons at C-7 generally absorb at higher field than those at C-11,[5a] it appears that the signal common to both spectra is due to a C-11 proton, whereas the variable signal is due to one at position 7. Molecular models indicate that as a result of the conformational changes induced in rings B and C by the double bond of the cholest-8(9)-ene-7,11-diol system, it is impossible for the proton at C-11 to give rise to a signal of half-band width as low as 6 Hz. This also indicates that the latter signal is due to a proton at position 7, and so again the signal common to both spectra is apparently due to a C-11 proton. Consequently, the hydroxy-group at this latter position is in the same configuration in both enediols, which must hence be merely epimeric at C-7. As a result of the skeletal deformations caused by the double bond,[5b] the observed positions of the 10- and 13-methyl resonances in these spectra do not agree particularly well with the calculated values [6] for any of



Scheme 1 Reagents: i, $AgOAc–I_2–HOAc–H_2O$; ii, $LiAlH_4$; iii, CrO_3–pyridine

[1] Part CCXIX, R. J. Liedtke, Y. M. Sheikh, A. M. Duffield, and C. Djerassi, *Org. Mass Spectrometry*, in the press.

[2] C. W. Davey, E. L. McGinnis, J. M. McKeown, G. D. Meakins, M. W. Pemberton, and R. N. Young, *J. Chem. Soc.* (*C*), 1968, 2674.

[3] J. C. Eck and E. W. Hollingsworth, *J. Amer. Chem. Soc.*, 1941, **63**, 2986.

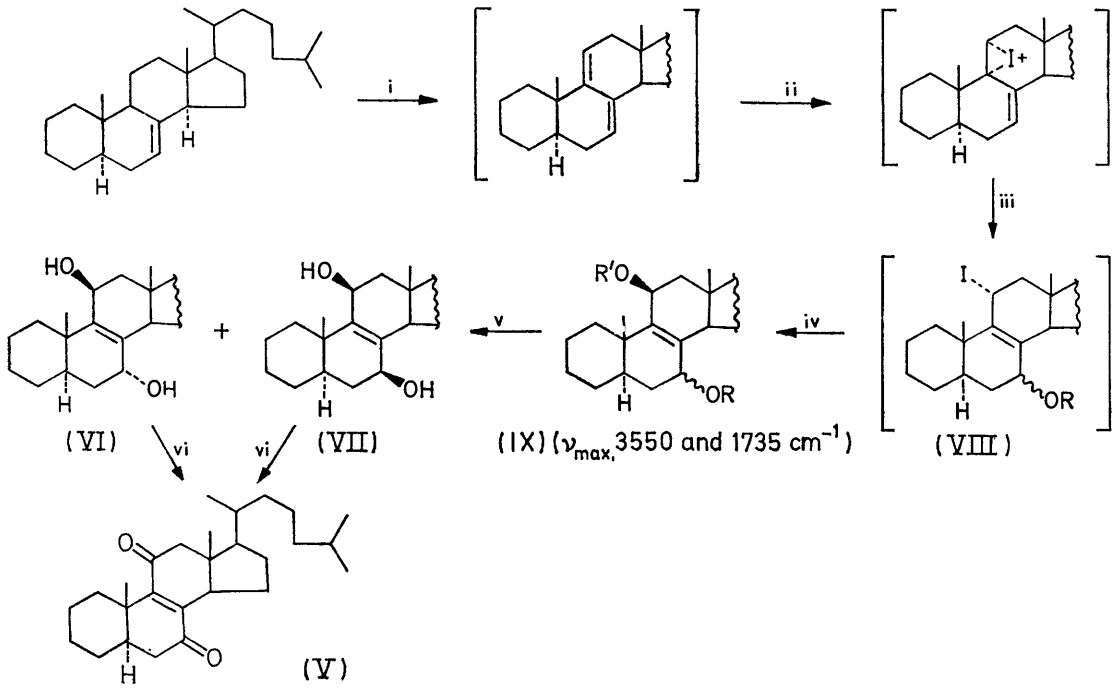
[4] G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarrett, *J. Amer. Chem. Soc.*, 1953, **75**, 422.

[5] N. S. Bhacca and D. H. Williams, 'Applications of NMR Spectroscopy in Organic Chemistry,' Holden-Day, San Francisco, 1964, (*a*) p. 84, (*b*) p. 25.

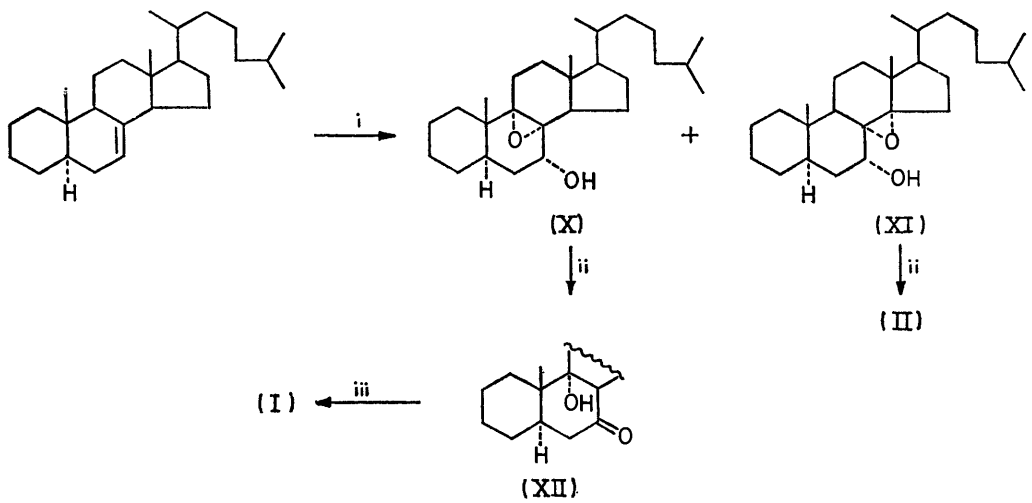
[6] R. F. Zürcher, *Helv. Chim. Acta*, 1963, **46**, 2054; see also ref. 6, p. 19.

the four possible isomers, but the structures which fit best are those of the $\Delta^{8(9)}$-7α,11β- (VI) and $\Delta^{8(9)}$-7β,11β- (VII) diols (see Experimental section); this lends further support to the foregoing conclusions.

the Simonini complex (AcOI, AcOAg),[2] then co-ordinates with I^+ as shown (*cf.* the manner in which such dienes form Δ^7-9α,11α-epoxides when treated with peroxy-acid [8]). Nucleophilic attack at C-7 by water or acetic



SCHEME 2 Reagents: i, I_2–AgOAc–HOAc–H_2O; ii, I^+; iii, ROH (R = H or Ac); iv, R'OH (R' = H or Ac); v, $LiAlH_4$; vi, CrO_3–pyridine



SCHEME 3 Reagents: i, *m*-$ClC_6H_4 \cdot CO_3H$; ii, H^+; iii, OH^-

Scheme 2 portrays what we consider to be the most probable mode of formation of the observed products. Dehydrogenation of Δ^7-steroids is known to be brought about by bromine,[7] or certain metal acetates [7] [*e.g.* $Hg(OAc)_2$, $Pb(OAc)_4$], so under the present conditions (iodine–silver acetate) such a transformation is also feasible. The resulting $\Delta^{7,9(11)}$-diene, in the presence of acid, from either face of the molecule, then generates the epimeric allylic iodides (VIII), which, on solvolysis, produce the unsaturated hydroxy-acetate mixture (IX; R = H, R' = Ac or *vice versa*). Stereospecific introduction of the C-11 oxygen function in this last reaction

[7] L. F. Fieser and M. Fieser, ' Steroids,' Reinhold, New York, 1959, p. 265.

[8] C. Djerassi, A. J. Lemin, G. Rosenkranz, and F. Sondheimer, *J. Chem. Soc.*, 1954, 2346; and P. Bladon, H. B. Henbest, E. R. H. Jones, G. W. Wood, G. C. Eaton, and A. A. Wagland, *ibid.*, 1953, 2916.

is neither invoked nor implied; the intermediate (IX) is represented as shown only because the products of its reduction with lithium aluminium hydride (VI) and (VII) both appear to possess 11β-hydroxy-groups.

Following an alternative route [that developed by Fieser *et al.*[9] for the preparation of the 3β-acetoxy-derivative of (II)] we treated 5α-cholest-7-ene with 2 mol. equiv. of peroxy-acid and isolated the resulting, isomeric epoxy-alcohols (X) and (XI). As in Fieser's series, of the two epoxides, the one with the lower m.p. and smaller (positive) rotation proved to be the 8α,14α-isomer (XI). Whereas one of these epoxides (XI) yielded an αβ-unsaturated ketone (II) upon rearrangement with acid, the other furnished a hydroxy-ketone, believed to be 9α-hydroxy-5α-cholestan-7-one (XII) (Scheme 3).

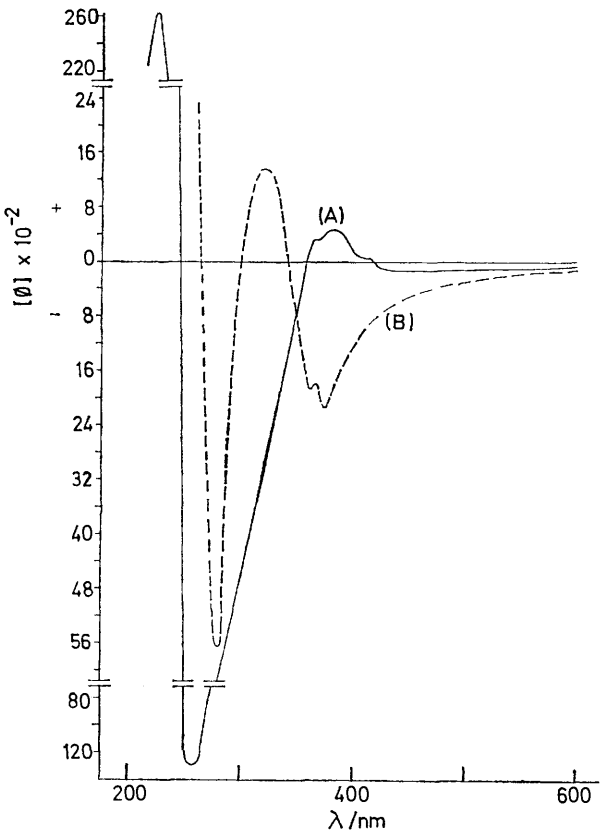
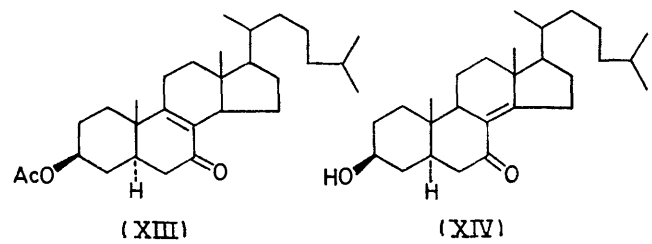


FIGURE O.r.d. curves of (A) 5α-cholest-8(9)-en-7-one and (B) 5α-cholest-8(14)-en-7-one

[9] L. F. Fieser, K. Nakanishi, and W.-Y. Huang, *J. Amer. Chem. Soc.*, 1952, **75**, 4719.

The transformation (XI) ⟶ (II) can be accounted for by invoking a cyclic transition state in the dehydration stage (Scheme 4), whereas in the other case, the stereochemistry of the enol form of the β-hydroxy-ketone (XII) is apparently such that dehydration is impossible (or extremely slow) under the (acidic) reaction conditions employed; however, refluxing compound (XII) in methanolic potassium hydroxide overnight did effect dehydration. Spectroscopic analysis of the samples of compounds (I) and (II) obtained *via* Scheme 3 provided complete and unequivocal proof of their authenticity. Thus, microanalysis and high resolution mass spectrometry yielded $C_{27}H_{44}O$ as the elemental composition of each compound; their i.r. and u.v. absorption spectra were essentially identical with those of simple derivatives [(XIII) and (XIV); see later] whose authenticities are beyond question; their n.m.r. spectra exhibited



SCHEME 4

(XIII) (XIV)

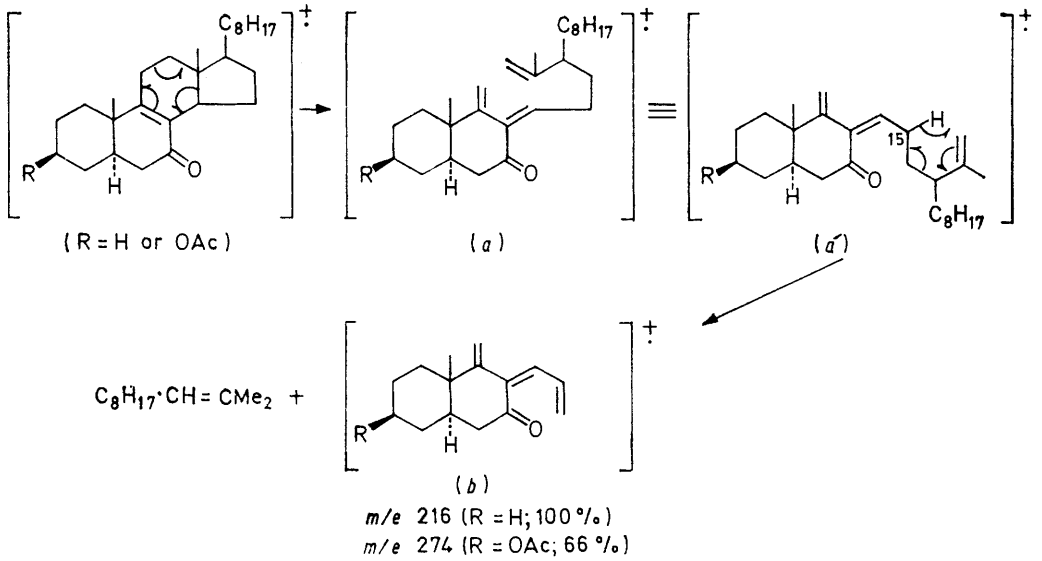
no signals in the olefin resonance region, and the positions of the 10- and 13-methyl signals were all within 0·02—0·04 p.p.m. of the values calculated by Zürcher's rules.[6] These latter values were computed from the additive chemical shifts of the appropriate C=C and 7-oxo entities, since the values for the two enones as conjugated chromophores were not available, and are hence subject to slight error.[6] The final (and most conclusive) pieces of evidence come from comparison of the electron-impact induced fragmentation patterns of these compounds with those of authentic derivatives (see later), and from the high degree of correspondence between the o.r.d. curve of each ketone (Figure) and those previously published of their 3β-acetate derivatives.[10] In addition, catalytic hydrogenation of the $\Delta^{8(14)}$-isomer (II) yielded a mixture of 5α-cholest-8(14)-ene and 5α-cholestan-7-one; this result has also been described in the 3β-acetoxy-series.[11]

The mass spectra of compounds (I) and (II) (prepared by Scheme 3) and of their 3β-oxygenated analogues

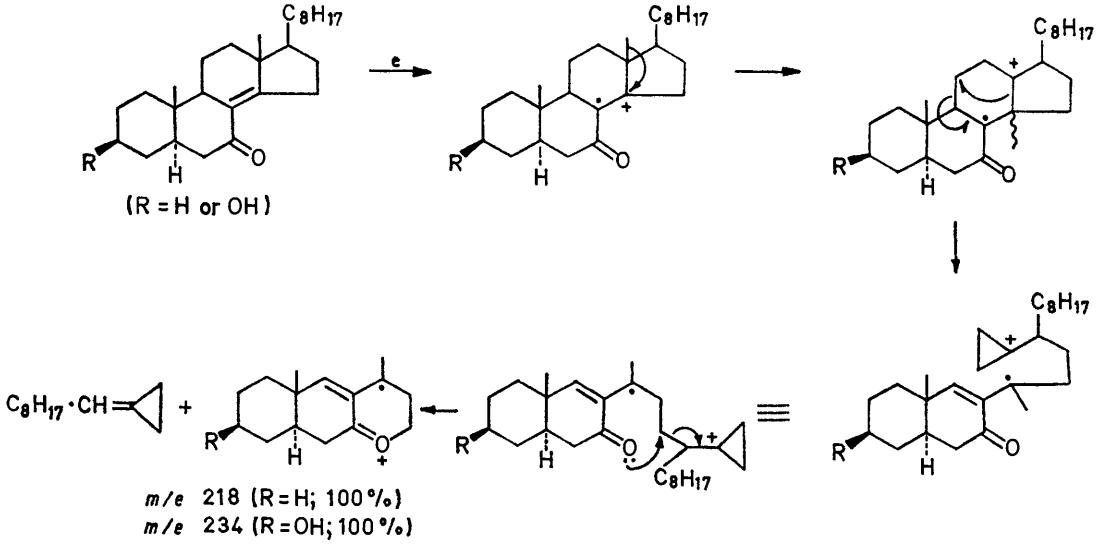
[10] C. Djerassi, R. Riniker, and B. Riniker, *J. Amer. Chem. Soc.*, 1956, **78**, 6377.

[11] O. Wintersteiner and M. Moore, *J. Amer. Chem. Soc.*, 1943, **65**, 1507.

(XIII) * and (XIV) [9] are deposited as Supplementary Publication No. SUP 20517 (2 pp., 1 microfiche).† Analysis of these spectra reveals that the outstanding difference between the behaviours of compounds (I) and (II) upon electron impact is also associated with the most favourable decomposition pathway in each case, and is therefore of considerable diagnostic importance. not involved in either of these fragmentation processes. High resolution mass measurements show that the neutral species lost is of a purely hydrocarbon nature in both cases [$C_{12}H_{24}$ in the $\Delta^{8(9)}$-enone series and $C_{12}H_{22}$ in the $\Delta^{8(14)}$ series], and metastable peak analysis indicates that all emanate directly from the appropriate molecular ion. Our proposed rationalisation (Scheme



SCHEME 5



SCHEME 6

Thus, the most intense fragment peak in the spectra of (I) and (II) occurs at *m/e* 216 and 218, respectively, whereas with their derivatives (XIII) and (XIV), these values are displaced by an amount equal to that introduced by substitution, thereby producing the *m/e* 274 and 234 peaks, respectively. It follows that ring A is 5) for the loss of $C_{12}H_{24}$ from the $\Delta^{8(9)}$-enones (I) and (XIII) following electron impact utilises all these data, and employs two consecutive, well-documented, cyclic rearrangement processes: retro-Diels–Alder (RDA) collapse of ring C [13] [⟶ (*a*)], followed by a McLafferty-

* We thank Professor Sir Ewart R. H. Jones, Oxford University, for supplying us with a sample of this compound, prepared by the method of ref. 12.

† For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

[12] E. R. H. Jones and D. J. Wluka, *J. Chem. Soc.*, 1959, 907.

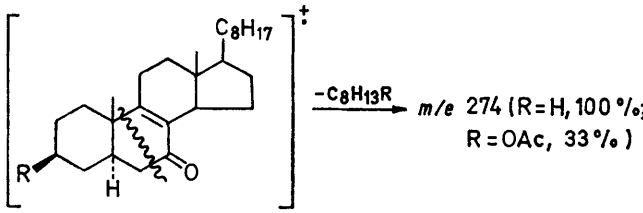
[13] For a review on the nature and occurrence of the RDA reaction in the mass spectra of organic compounds (in particular, unsaturated steroids and pentacyclic triterpenoids) see H. Budzikiewicz, J. I. Braumann, and C. Djerassi, *Tetrahedron*, 1965, **21**, 1855.

style transfer of a C-15 hydrogen to the outgoing portion of the molecule * [(*a'*) ⟶ (*b*)].

The low-intensity peak 2 mass units higher than ion (*b*) in these spectra indicates that migration of the double bond to the 8(14)-position precedes fragmentation to a small extent (see later).

Less easily rationalised is the mode of formation of the diagnostic $M - C_{12}H_{22}$ ion in the spectra of the $\Delta^{8(14)}$-enones (II) and (XIV). RDA rearrangement in these cases would result in the expulsion of a neutral ethylene molecule, with concomitant formation of a cyclopentene derivative. No $M - C_2H_4$ peak can be detected in either spectrum, and the $M - 168$ peak noted before is also absent, so it appears that the RDA process does not occur in these spectra, with or without prior migration of the double bond to the 8(9)-position. Therefore, a totally different mechanism must be operative, and in view of the known ability of a methyl group situated γ to the carbonyl group of a cyclic $\alpha\beta$-unsaturated ketone to undergo a 1,2-shift following electron impact,[15] we propose that such a process triggers the loss of $C_{12}H_{22}$ in these spectra (Scheme 6). If this is correct, then migration of a methyl group, in this instance, must be energetically more favourable than the RDA reaction.

Another difference between the mass spectra of these enones lies in the ability of the $\Delta^{8(9)}$-ketones (I) and (XIII) to undergo the ring B fragmentation shown, whereas the $\Delta^{8(14)}$-isomers (II) and (XIV) are incapable of this. At first sight, this is unexpected, since the 9,10-bond is vinylic in the former case and allylic in the latter; presumably, skeletal rearrangements must be intervening after ionisation in order to facilitate such



fragmentation modes. In the absence of suitable precedents, any proposed mechanism would be highly speculative.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. U.v. spectra were recorded for solutions in absolute ethanol with a Cary model 14 spectrometer; i.r. spectra were obtained for solutions in chloroform with a Perkin-Elmer 421 spectrometer. ^{1}H N.m.r. spectra were determined with deuteriochloroform as solvent and tetramethylsilane as internal reference on a Varian HA-100 spectrometer. Routine optical rotations were recorded with a Perkin-Elmer model 141 spectropolarimeter for solutions in chloroform; o.r.d. curves were determined for solutions in dioxan by Mrs. R. Records (whom we thank) with a JASCO ORD/UV 5 spectrometer with c.d. attachment. Microanalyses were performed by Messrs E. Meier and J. Consul. Low resolution mass spectra were determined by Messrs R. G. Ross and R. Conover with A.E.I. MS9 and Atlas CH-4 spectrometers operating at 70 eV, by use of the direct inlet system. High resolution measurements were obtained with the MS-9 instrument on-line to the ACME computer facilities of Stanford University Medical Center.

The progress of all reactions and column chromatographies (Merck alumina, activity II) was monitored by t.l.c. on silica gel (HF_{254}) microplates. Benzene was used as developing solvent, and spots were detected by spraying with a 2% solution of cerium(IV) sulphate in 2N-sulphuric acid, followed by heating.

5α-Cholest-7-ene.—Cholesta-5,7-dien-3β-yl benzoate (Dawes Laboratories) (25 g) was saponified (5% KOH–MeOH). Subsequent catalytic hydrogenation (Raney nickel–dioxan), tosylation (toluene-*p*-sulphonyl chloride–pyridine), and reduction (lithium aluminium hydride–ether), followed by chromatography on alumina in hexane, and recrystallisation gave 5α-cholest-7-ene (15 g, 80% overall yield), m.p. 86—87°, $[\alpha]_D^{20}$ +10·5° (*c* 1·1) (lit.,[16] m.p. 86—87°, $[\alpha]_D^{20}$ +11°), *M* (mass spectrum) 370 ($C_{27}H_{46}$).

Reaction of 5α-Cholest-7-ene with Iodine–Silver Acetate.—The procedures described in ref. 2 for the preparation of the supposed intermediates (III) and (IV) were followed exactly; our products exhibited the following properties: 5α-cholest-8-ene-7α,11β-diol (VI), m.p. 167—169°, $[\alpha]_D^{20}$ +39° (*c* 0·8) {lit.[2] for '(III)': m.p. 171—173°, $[\alpha]_D^{20}$ +42°}, δ 4·47 (11α-H, $W_{\frac{1}{2}}$ *ca.* 14 Hz), 4·04 (7β-H, $W_{\frac{1}{2}}$ *ca.* 6 Hz), 0·82 (3H, s, 18-H_3; calc.[6] 0·809), and 1·12 p.p.m. (3H, s, 19-H_3; calc.[6] 1·150), *m/e* 402 (M^+; 4% at 70 eV, 14% at 15 eV) and 384 ($M - H_2O$; 100% at both 15 and 70 eV); 5α-cholest-8-ene-7β,11β-diol (VII), m.p. 199—201°, $[\alpha]_D^{20}$ +125° (*c* 1·1) {lit.[2] for '(IV)': m.p. 206—207°, $[\alpha]_D^{20}$ +130°}, δ 4·47 (11α-H, $W_{\frac{1}{2}}$ *ca.* 14 Hz), 4·07 (7α-H, $W_{\frac{1}{2}}$ *ca.* 12 Hz), 0·87 (3H, s, 18-H_3; calc.[6] 0·834), and 1·02 p.p.m. (3H, s, 19-H_3; calc.[6] 1·183), *m/e* 402 (M^+; 2% at 70 eV, 9% at 15 eV) and 384 ($M - H_2O$; 100% at both 15 and 70 eV).

Samples of compounds (VI) and (VII) were oxidised with chromium trioxide in pyridine as described,[2] and the single product (V) obtained in each case was recrystallised several times from methanol to give lemon-coloured needles of 5α-cholest-8-ene-7,11-dione, m.p. 115—116°, $[\alpha]_D^{20}$ +60° (*c* 1·0), $\nu_{C=O}$ 1680 cm^{-1}, $\lambda_{max.}$ 267 nm (ε 6900),† δ 0·68 (3H, s, 18-H_3; calc.[6] 0·683) and 1·30 p.p.m. (3H, s, 19-H_3; calc.[6] 1·283), *M* (mass spectrum) 398 ($C_{27}H_{42}O_2$) {lit.[2] for '(II)': m.p. 118—118·5°, $[\alpha]_D^{20}$ +59°, $\nu_{C=O}$ 1680 cm^{-1}, $\lambda_{max.}$ 267 nm (ε 7600)}.

8α,9α- and 8α,14α-Epoxy-5α-cholestan-7α-ols [(X) *and* (XI)].—5α-Cholest-7-ene (15 g) was added in portions to a cooled, stirred solution of *m*-chloroperoxybenzoic acid (17 g, 85%) (Aldrich) in chloroform (350 ml) at 13 ± 2 °C. After 8 days at 0—5°, the mixture was filtered, and the solution washed successively with 5% solutions of sodium hydrogen sulphite and sodium hydrogen carbonate. Evaporation of

* McLafferty rearrangements have recently[14] been shown to operate in the mass spectra of olefins.

† Dorfmann's review on steroid u.v. absorption spectra (*Chem. Rev.*, 1953, **53**, 47) gives 253 (11,200), 262 (9500), and 270 nm (7400) as the mean $\lambda_{max.}$ (ε) values for various derivatives of (I), (II), and (V), respectively.

[14] M. Kraft and G. Spiteller, *Org. Mass Spectrometry*, 1969, **2**, 865; K. K. Mayer and C. Djerassi, *ibid.*, 1971, **5**, 817.

[15] R. L. N. Harris, F. Komitsky, and C. Djerassi, *J. Amer. Chem. Soc.*, 1967, **89**, 4765.

[16] G. M. L. Cragg, C. W. Davey, D. N. Hall, G. D. Meakins, E. E. Richards, and T. L. Whateley, *J. Chem. Soc.* (*C*), 1966, 1266.

the dried ($MgSO_4$) solution yielded an oil which was chromatographed on alumina (800 g). Elution with n-hexane and 10% ether–hexane yielded small amounts of starting material and an unidentified impurity; elution with 15 and 20% ether–hexane produced first the 8α,14α-*epoxide* (XI), m.p. 93—94°, $[\alpha]_D^{20}$ +9·5° (*c* 0·8), δ 3·55 (1H, m, 7β-H), 0·92 (3H, s, 18-H_3), and 0·86 (3H, s, 19-H_3) (Found: C, 80·6; H, 11·5%; M^+, 402. $C_{27}H_{46}O_2$ requires C, 80·6; H, 11·4%; *M*, 402); and then the 8α,9α-*isomer* (X), m.p. 131—132°, $[\alpha]_D^{20}$ +43° (*c* 1·2), δ 3·90 (1H, m, 7β-H), 0·97 (3H, s, 18-H_3), and 0·65 p.p.m. (3H, s, 19-H_3) (Found: C, 80·5; H, 11·3%; M^+, 402).

Acid-catalysed Rearrangement of the Epoxides (X) *and* (XI).—The epoxide (X) (1 g), ethanol (40 ml), and 36% hydrochloric acid (4 ml) were heated under reflux for 3 h; the solution was then diluted with water to saturation at the b.p. and cooled in ice. The product was filtered off, washed, and recrystallised to yield 9α-*hydroxy*-5α-*cholestan*-7-*one* (XII), m.p. 205—206° (from ethyl acetate), $[\alpha]_D^{20}$ −59° (*c* 0·9), $\nu_{max.}$ 3500 (O–H) and 1705 (C=O) cm^{-1}, δ 0·66 (3H, s, 18-H_3; calc.[6] 0·650) and 1·16 p.p.m. (3H, s, 19-H_3; calc.[6] 1·180) (Found: C, 80·9; H, 11·3%; M^+, 402. $C_{27}H_{46}O_2$ requires C, 80·6; H, 11·4%; *M*, 402). Similarly the epoxide (XI) gave 5α-*cholest*-8(14)-*en*-7-*one* (II), m.p. 85—86°, $[\alpha]_D^{20}$ −53° (*c* 1·0), $\nu_{C=O}$ 1665 cm^{-1}, $\lambda_{max.}$ 261 nm (ε 9200),† δ 0·79 (3H, s, 18-H_3; calc.[6] 0·825) and 0·89 p.p.m. (3H, s, 19-H_3; calc.[6] 0·933) (Found: C, 84·4; H, 11·4. $C_{27}H_{44}O$ requires C, 84·4; H, 11·5%), *m/e* 384 (M^+, $C_{27}H_{44}O$; 100%), 369 ($M - CH_3$; 9%), 274 ($M - C_8H_{14}$; 2%), 271 ($M - C_8H_{17}$; 23%), 257 ($M - C_9H_{19}$; 7%), 246 ($M - C_{10}H_{18}$; 6%), 243 ($M - C_{10}H_{21}$; 7%), 229 ($M - C_{11}H_{23}$; 9%), and 218 ($M - C_{12}H_{22}$; 53%) (all other peaks above *m/e* 200 <5%). The mass spectrum of the 3β-hydroxy-derivative (XIV) of (II), prepared according to ref. 9, had *m/e* 400 (M^+, $C_{27}H_{44}O_2$; 100%), 384 ($M - CH_3$; 13%), 287 ($M - C_8H_{17}$; 47%), 274 ($M - C_8H_{14}O$; 2%), 273 ($M - C_9H_{19}$; 14%), 262 ($M - C_{10}H_{18}$; 12%), 259 ($M - C_{10}H_{21}$; 11%), 245 ($M - C_{11}H_{23}$; 17%), and 234 ($M - C_{12}H_{22}$; 79%) (all other peaks above *m/e* 200 <10%).

5α-*Cholest*-8(9)-*en*-7-*one* (I).—9α-Hydroxy-5α-cholestan-7-one (XII) (250 mg), potassium hydroxide (500 mg), and methanol (20 ml) were heated under reflux for 20 h. The solution was then diluted; the product was filtered off, washed, dried, and recrystallised from ethyl acetate to give *plates*, m.p. 118—119°, $[\alpha]_D^{20}$ −24° (*c* 0·7), $\nu_{C=O}$ 1660 cm^{-1}, $\lambda_{max.}$ 252 nm (ε 10,200) † {lit.[2] for ' (I) ': m.p. 86—88°, $[\alpha]_D^{20}$ +4°, $\nu_{C=O}$ 1680 cm^{-1}, $\lambda_{max.}$ 252 nm (ε 11,800)}, δ 0·59 (3H, s, 18-H_3; calc.[6] 0·567) and 1·15 p.p.m. (3H, s, 19-H_3; calc.[6] 1·175) (Found: C, 84·2; H, 11·6. $C_{27}H_{44}O$ requires C, 84·4; H, 11·5%), *m/e* 384 (M^+, $C_{27}H_{44}O$; 100%), 369 ($M - CH_3$; 13%), 274 ($M - C_8H_{14}$; 22%), 271 ($M - C_8H_{17}$; 22%), 244 ($M - C_{10}H_{20}$; 13%), 229 ($M - C_{11}H_{23}$; 30%), 218 ($M - C_{12}H_{22}$; 19%), 216 ($M - C_{12}H_{24}$; 55%), and 203 ($M - C_{13}H_{25}$; 12%) (all other peaks above *m/e* 200 <10%). The mass spectrum of the 3β-acetoxy-derivative (XIII) of (I) [12] had *m/e* 442 (M^+, $C_{29}H_{46}O_3$; 100%), 427 ($M - CH_3$; 14%), 329 ($M - C_8H_{17}$; 25%), 302 ($M - C_{10}H_{20}$; 13%), 287 ($M - C_{11}H_{23}$; 20%), 276 ($M - C_{12}H_{22}$; 26%), 274 ($M - C_{12}H_{24}$, 41%; and $M - C_{10}H_{16}O_2$, 21%), and 214 ($M - C_{14}H_{28}O_2$; 21%) (all other peaks above *m/e* 200 <10%).

Catalytic Hydrogenation of 5α-*Cholest*-8(14)-*en*-7-*one* (II).—The enone (250 mg), 5% palladium–charcoal (80 mg), and ethyl acetate (40 ml) were stirred for 20 h at room temperature under 1 atm of hydrogen (uptake 25 ml, 1·55 mol. equiv.). After filtration, the solution was evaporated to dryness and the residue chromatographed. Elution with n-hexane yielded 5α-cholest-8(14)-ene (75 mg); elution with 10% benzene–hexane afforded 5α-cholestan-7-ene (115 mg). Both products were identified by m.p. and mixed m.p., optical rotation, and comparison of their n.m.r. and mass spectra with those of authentic specimens.‡

We thank the National Institutes of Health, U.S. Public Health Service, for financial assistance.

[2/1230 *Received*, 1*st June*, 1972]

† See footnote p. 2775.

‡ 5α-Cholest-8(14)-ene was prepared by rearrangement of the Δ^7-isomer under catalytic hydrogenation conditions (Pt–HOAc) in a similar manner to that described in ref. 16 for the synthesis of 5α-ergost-8(14)-ene; 5α-cholestan-7-one also was prepared by the procedures outlined in ref. 16.