DEGRADATION OF SOME QUATERNARY DERIVATIVES OF RING-B SUBSTITUTED AMINOCHOLESTANES

HOFMANN VS. SAYTZEFF ORIENTATION IN THE ELIMINATION REACTIONS[1]

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Abstract—Degradation of *ax*-7α-cholestanyltrimethylammonium iodide under neutral and alkaline conditions gives mainly cholest-7-ene and cholest-6-ene respectively. Degradation of the amine oxides derived from 6α-, 6β-, and 7α-dimethylaminocholestanes gives in all three cases cholest-6-ene almost exclusively. The results are discussed and compared with previous observations.

ALKALINE degradation, usually by the E2 mechanism, of acyclic quaternary ammonium salts normally leads to the Hofmann olefin by preferential base attack on hydrogen attached to the least alkylated β-carbon atom.[2] Until recently the preferential formation[3] of menth-3-ene (I) by E2 degradation of neomenthyltrimethylammonium salts (II) has been regarded as a rather unusual result, but there now seem to be in the literature[4] enough examples of formation of the Saytzeff product in alkaline eliminations with alicyclic quaternary ammonium salts to make it evident that the Hofmann rule will often not be followed in such cases. The most extreme example[4a] is the degradation of 6β-cholestanyltrimethylammonium salts (V; $R = \overset{+}{N}Me_3\overset{-}{X}$), where none of the Hofmann product, cholest-6-ene (IX) has been observed in the product, essentially pure cholest-5-ene (VIII). The alkaline degradation of V($R = \overset{+}{N}Me_3\overset{-}{X}$) undoubtedly follows the E2 mechanism: a detailed kinetic study has not been made (see following paper) but the degradation rate increases markedly in presence of added alkali hydroxide, and this increase can hardly be explained by intervention of an E1cB or an $\alpha^1\beta$ mechanism in the relevant structural circumstances.

That kinetically E2 processes with $>CX—CH<$ can involve a range of transition-state types varying from near-E1 to near E1cB, depending on whether fission of C—X or C—H is in the lead, is now a well accepted principle; the variation for different substrates and bases can be examined *inter alia* by analysis of product ratios or kinetic isotope effects. A near-E1 type of transition state for the E2 reaction of the neomenthyl salts has been held[3] by Hughes *et al.* to be responsible for the predominance of the Saytzeff product (I), which is also the product of E1 elimination with the

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[1] Some of the results have been communicated in preliminary form: R. Ledger and J. McKenna, *Chem. & Ind.* 738 (1963); R. Ledger, P. B. Smith and J. McKenna, *Ibid* 863 (1963).

[2] For recent reviews of elimination reactions see J. F. Bunnett, *Angewandte Chemie* (*International Ed.*) 1, 225 (1962); D. V. Banthorpe, *Elimination Reactions*. Elsevier, Amsterdam (1963).

[3] E. D. Hughes and J. Wilby, *J. Chem. Soc.* 4094 (1960), and Refs quoted therein.

[4a] B. B. Gent and J. McKenna, *J. Chem. Soc.* 137 (1959);

[5] T. H. Brownlee and W. H. Saunders, Jr. *Proc. Chem. Soc.* 314 (1961).

quaternary iodide in a neutral solvent. This explanation is applicable *a fortiori* to the 6β-cholestanyl salt, El degradation with which is much faster than with the neomenthyl salt, taking place quite rapidly in boiling neutral ethanol under which conditions the neomenthyl salt would apparently[3] be unaffected. An alternative explanation, based on Brown's orientation theory,[5] would be that since base approach to the axial 5α- and 7α-hydrogen atoms in the 6β-quaternary salt is approximately equally easy (cf. Fig. XI, which illustrates the different steric environments of axial groups or hydrogen atoms at C-5,-6,-7, and -8), this being the most relevant consideration from Brown's theory with such alicyclic systems, the outcome of the E2 reaction (irrespective of transition state type) would be determined by the extra stability of the developing 5:6 (*vs.* a developing 6:7) olefinic linkage. As each extreme orientation theory indicates the same probable result for an E2 reaction of the 6β-cholestanyltrimethylammonium salt, it seemed to be of interest to examine the corresponding process with the analogous (axial) 7α-salt (VI, R $= \overset{+}{N}Me_3\overset{-}{X}$). With this salt the relevant transition state would probably also have El characteristics, which should lead, by one theory, to a tendency to predominant cholest-7-ene (X) formation; however, base approach, shielded by only one axial methyl group (cf. XI), to the axial 6-hydrogen atom should be much easier[6] than approach (shielded by two methyl groups) to the axial 8-hydrogen atom, a circumstance which by the other orientation theory would tend to result in predominant formation of cholest-6-ene (IX) in an E_2 reaction.

The preparation of the relevant 7-aminocholestanes and their derivatives, with comments on some discrepancies between our results and those of other authors,[7,8] is described in the Experimental Section. In the event, it was found that the ax-7α-trimethylammonium salt was degraded to olefin (nearly pure cholest-7-ene, as expected) fairly rapidly in boiling neutral ethanol; this is undoubtedly an El process, so that the transition state of the corresponding E2 process, which is (see following paper) what is being observed in the much more rapid degradation of the iodide in alkaline ethanol (and under other basic conditions) should have more strongly developed El characteristics than the transition state for the analogous E2 reaction of the neomenthyl salt. However, the alkaline degradations yielded mainly cholest-6-ene which was under some conditions almost the exclusive olefinic product. While it seems clear that the above steric explanation, formally an application of Brown's orientation theory, is required to explain the observed orientation in the alkaline eliminations, it should be pointed out that Ingold's school also admits[9] a possibility of the relevant steric effect in quaternary salts of adequate complexity.*

Since the 7-axial trimethylammonium group is not opposed by a 1:3 diaxial interaction with C-methyl, neither the neutral nor the alkaline degradation of the 7α-salt is as fast as the corresponding reaction of the 6β-analogue. The 7-axial salt is, however, degraded more rapidly than the neomenthyl salt, probably because of the

* According to Ingold *et al.*,* steric compression between base and substrate might arise in "gargoyle" molecules. Following this nomenclature, it appears from our results that the β-face of the cholestane nucleus, but not the α-, might be said to be "gargoyle"!

[5] H. C. Brown and I. Moritani, *J. Amer. Chem. Soc.* **78**, 2203 (1956).

[6] cf. E. J. Corey and R. A. Sneen, *J. Amer. Chem. Soc.* **78**, 6269 (1956).

[7] C. W. Shoppee, R. J. W. Cremlyn, D. E. Evans and G. H. R. Summers, *J. Chem. Soc.* 4364 (1957).

[8] C. W. Bird and R. C. Cookson, *J. Chem. Soc.* 2343 (1960).

[9] D. V. Banthorpe, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.* 4054 (1960).

rigidity of the cholestane ring-B in comparison with that of the isolated cyclohexane ring (a factor increasing the 1:3 diaxial interactions in the steroidal salt) and because additionally of the larger number of hydrogen atoms in 1:3-opposition to the axial-$\overset{+}{N}Me_3$ group in the steroid (3 as compared with 2 in the terpenoid). In this paper, however, we are mainly concerned with *orientation* in the elimination reactions: *differential rates* of these and other processes are discussed in the following paper.[10] The discussion there includes examination of the difficulty of making quaternary derivatives of the *eq*-7β-dimethylaminocolestane (VII; R = NMe$_2$) although it happens to be convenient to quote the (attempted) preparational details in this paper, as they are analogous to those used with the axial analogue.

We also examined the reactions of the four ring-B dimethylaminocholestanes towards N-oxidation reagents, and the decomposition of the N-oxides.[11] With hydrogen peroxide in refluxing methanol[12] 6α-dimethyl-aminocholestane (IV; R = NMe$_2$) evidently was converted into the N-oxide (IV; R = $\overset{+}{N}Me_2\overset{-}{O}$) although only the olefinic decomposition product from this (mainly cholest-6-ene) was in fact isolated. There was no definite evidence that any of the other three bases were converted even partially into N-oxides under the same conditions, but the reactions were not smooth: some base was in each case recovered (as hydrochloride) and unidentified oils were also produced. We therefore examined the action of the peracetic acid. With 6α-dimethylaminocholestane the amine oxide was readily formed and isolated; it gave almost pure cholest-6-ene on pyrolysis. The same hydrocarbon was formed from the 6β- and 7α-isomers (V and VI; R = NMe$_2$), but in this case the evidently less stable N-oxides (V and VI; R = $\overset{+}{N}Me_2\overset{-}{O}$) were not isolated, but decomposed under the conditions of their formation (at room temp) or, more likely, during workup. The 7β-tertiary base (VII; R = NMe$_2$), treated under the same conditions, was largely recovered.

Two points of interest emerge from these experiments—firstly, the variation in apparent ease of N-oxide formation for the series of bases, particularly the order 7α(*ax*) > 7β(*eq*) (see following paper[10]) and, secondly, the almost exclusive formation of cholest-6-ene from the 6α-oxide, especially when this was isolated (following peracetic acid oxidation) and pyrolysed. The 6-ene is of course the only hydrocarbon expected from the 6β- and the 7α-isomeric amine oxides, as a 1:2-diaxial grouping of 5α-H and 6β-$\overset{+}{N}Me_2\overset{-}{O}$, or 8β-H and 7α-$\overset{+}{N}Me_2\overset{-}{O}$ (Fig. XI) could not lead to the preferred *syn*-periplanar type of transition state for the Ei reaction. The 6α-$\overset{+}{N}Me_2\overset{-}{O}$ group also appears to avoid internal elimination with the 5α-H, although in a formally analogous case,[13] *viz*, the decomposition of menthyldimethylamine oxide (III), 36% of the hydrocarbon product is menth-3-ene (I). While ring B in cholestane is of course as a whole much more rigid than the isolated cyclohexane ring in the terpene derivative, the particular high rigidity at C-5 in IV, because of the ring fusion, which makes it *especially* difficult for the 5α-H to be part of a truly *syn*-periplanar transition

[10] J. McKenna, J. M. McKenna, R. Ledger and P. B. Smith, *Tetrahedron* 20, 2423 (1964).
[11] For a recent review of the Cope reaction see A. C. Cope and E. R. Trumbull, *Organic Reactions* 11, 317 (1960).
[12] cf. B. B. Gent and J. McKenna, *J. Chem. Soc.* 573 (1956).
[13] A. C. Cope and E. M. Acton, *J. Amer. Chem. Soc.* 80, 355 (1958).

state (with a dihedral angle of 0° between C_5-H and C_6-N), may be responsible for the observed result.

Apart from theoretical interest, the experimental work described in this paper provides the basis of convenient syntheses for the rather inaccessible cholest-6- and -7-ene (IX and X respectively), possibly most readily through alkaline and neutral degradations of the 7α-quaternary salt (VI; R = $\overset{+}{N}Me_3\overset{-}{I}$).
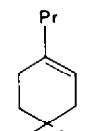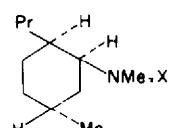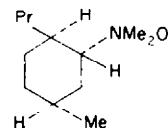
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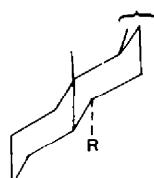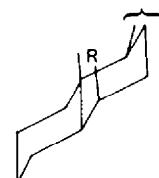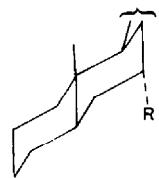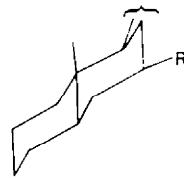
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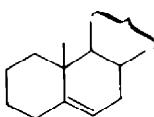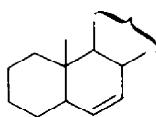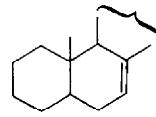
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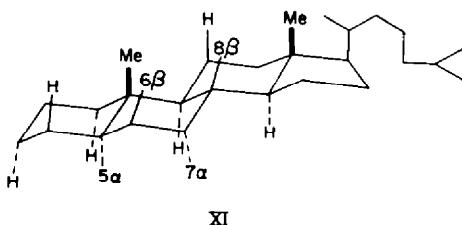
XI

EXPERIMENTAL

Optical rotations were determined in chloroform at room temp (ca. 20°) at concentrations of 0·5–2% using an ETL–NPL automatic polarimeter, type 143A, with a 0·2 dm cell. Light petroleum

refers to the fraction of b.p. 40–60°. Physical characteristics quoted for pure cholestenes are taken from Fieser and Fieser[14] (m.ps, $[\alpha]_D$) and from papers by Henbest et al.[15] (spectroscopic data).

7α- and 7β-Aminocholestane and derivatives

Cholestan-7-one was prepared from cholesterol via cholesta-3:5-dien-7-one using the modified route described by Nickon and Bagli.[16] The oxime, m.p. 133–135°, was reduced with sodium in boiling pentanol or with LiAlH₄ in boiling ether, following procedures described by other authors;[7,8] a mixture of 7α- and 7β-aminocholestanes, the latter predominating, was obtained by the first method, and 7α-aminocholestane occasionally admixed with a few percent of the equatorial epimer, by the second. These bases were readily separated by use of the fact that the axial (7α) primary hydrochloride is readily soluble in, and the epimeric equatorial (7β) hydrochloride almost insoluble in, ether or light petroleum. Primary amines were methylated to N,N-dimethyl-tertiary bases by the formaldehyde–formic acid method (the use of which for other bases is described e.g. in Ref. 4a).

Methylation of 7α-dimethylaminocholestane (or the primary amine) with methyl iodide gave the corresponding trimethylammonium salt, sometimes (depending on reaction conditions) admixed with olefin formed by degradation of the quaternary salt. For example, a solution of 7α-aminocholestane (0·67 g) in methyl iodide (3 ml) and methanol (1 ml) was refluxed with finely powdered K₂CO₃ (1 g) for 12 hr, the mixture was evaporated to dryness, and the residue was extracted with chloroform. The light-petroleum insoluble fraction (0·51 g) of the residue was the 7α-trimethylammonium salt, while the light-petroleum soluble fraction was separated after treatment with HClaq into steroidal olefin (60 mg) and tertiary base hydrochloride (90 mg).

A solution of 7β-dimethylaminocholestane (0·31 g) in methyl iodide (3 ml) and acetone (1 ml) was refluxed with excess of solid K₂CO₃ for 18 hr; the base was virtually unchanged by this treatment, although small yields of neutral product (possibly steroidal olefin: see below) were produced by prolonged reflux. The base (0·12 g) in methyl iodide (3 ml) was heated with finely powdered K₂CO₃ (1 g) in an autoclave at 100° for 4 days; the mixture was then evaporated and the residue was extracted with chloroform; the extract was separated into a fraction (24 mg) insoluble in, and a fraction (94 mg) soluble in, light petroleum. The former had m.p. 204–206°, $[\alpha]_D$ +37° after recrystallization from acetone, and was identified as 7β-dimethylaminocholestane hydriodide by comparison (mixed m.p. and IR spectra) with an authentic specimen, m.p. 202–204°, $[\alpha]_D$ +38°. With cold K₂CO₃aq, this salt immediately yielded the tertiary base; evidently, however, the solid carbonate was not completely effective in preventing hydriodide formation under the conditions of the autoclave experiment (no mixing by reflux). The petroleum-soluble fraction was separated with HClaq into 7β-dimethylaminocholestane hydrochloride (38 mg) and a neutral fraction, m.p. 134–136°, $[\alpha]_D$ −42° ν_{max}^{KBr} 492, 506 cm⁻¹ (strong; possibly attributable[17] to a carbon–iodine linkage) 795 and 827 cm⁻¹ (weak; attributed to cholest-7-ene). (Found: C, 67·0; H, 9·5; I, 24·1. Calc. for C₂₇H₄₇I: C, 65·1; H, 9·5; I, 25·5%). Reduction of this fraction, apparently mainly the iodide, with sodium in boiling pentanol for 1 hr gave cholestane which was pure after one recrystallization from methanol, and was identified by mixed m.p. (77–79°) and IR spectrum (Found: C, 87·4; H, 13·1. Calc. for C₂₇H₄₈: C, 87·0; H, 13·0%).

Physical properties and elemental analyses of derivatives of the 7-aminocholestanes are given in Table 1, which for comparison includes data provided by other authors. Some discrepancies in properties and in preparational details may be noted as follows: Bird and Cookson[8] imply that 7α-aminocholestane hydrochloride is insoluble in ether, their salt being precipitated from a solution of the base in dry ether. We find, however, that the dry hydrochloride (unlike its epimer) is readily soluble in cold dry ether. The discrepancy here may be more apparent than real, and due to differences in exact experimental conditions. Shoppee et al. quote a m.p. of 168–172° for cholestan-7-one oxime, while our samples have m.p. 133–135°, in agreement with the value (134–135°) quoted by Eck and Hollingsworth.[18] In correspondence, Professor Shoppee and Dr. Summers kindly

[14] L. F. and M. Fieser, Steroids p. 253. Reinhold, New York (1950).

[15] P. Bladon, J. M. Fabian, H. B. Henbest, H. P. Koch and G. W. Wood, J. Chem. Soc. 2402 (1951); H. B. Henbest, G. D. Meakins and G. W. Wood, Ibid. 800 (1954).

[16] A. Nickon and J. F. Bagli, J. Amer. Chem. Soc. 83, 1498 (1961).

[17] L. J. Bellamy, The Infra-red Spectra of Complex Molecules (2nd Edition) p. 332. Methuen, London (1958).

[18] J. C. Eck and E. W. Hollingsworth, J. Amer. Chem. Soc. 63, 2986 (1941).

informed us that there is some evidence that the oxime may be polymorphic, sometimes showing a double m.p. 138/168°, but we have not encountered this behaviour with our samples.

The most serious discrepancies (on which we can offer no comment) in the reported physical properties (Table 1) relate to 7α- and 7β-acetamidocholestanes; for the 7α-isomer there is a ca. 55° variation in $[\alpha]_D$ and for the 7β-isomer a ca. 65° variation in m.p. between values for corresponding samples prepared by Professor Shoppee's group and our own.

Degradation of 7α-cholestanyltrimethylammonium salts

Details of degradations carried out under a variety of conditions are given in Table 2. In each case the light petroleum or ether-soluble product was treated with HClaq and recovered base was isolated as hydrochloride, which was identified by comparison with an authentic specimen. The quoted approximate analyses for percentages of cholest-7-ene in the -6-ene/-7-ene mixtures (which formed the neutral reaction products) are based on $[\alpha]_D$ measurements on the *crude* hydrocarbon mixtures; IR examination of these crude mixtures supported the approximate proportions indicated. Pure cholest-6-ene has m.p. 87°, $[\alpha]_D$ −88°, with ν_{max} for a 6-ene ca. 770 cm⁻¹, while pure cholest-7-ene has m.p. 87°, $[\alpha]_D$ +12°, ν_{max} 795 and 825 cm⁻¹.

The cholest-7-ene from degradation in natural ethanol was analysed (Found: C, 87·9; H, 12·1. Calc. for $C_{27}H_{46}$: C, 87·5; H, 12·5%), as was the cholest-6-ene from a degradation in alkaline ethanol (Found: C, 87·9; H, 12·4%). The latter, on hydrogenation in ether–acetic acid over a Pt catalyst, gave cholestane, identified by mixed m.p. (78–80°) and IR spectrum.

Degradation of the quaternary salt in boiling chloroform gave trimethylammonium hydriodide as an insoluble precipitate (identified by mixed m.p., 232–240°, and IR spectrum) and a neutral product, m.p. 78–79°, raised to 88–89° after one recrystallization from acetone, $[\alpha]_D$ of crude product, −19°, which appeared from its elemental analysis (Found: C, 77.9; H, 11.2; I, 10.6%) and IR spectrum (ν_{max}^{KBr} 492,506,795,825 cm⁻¹) and $[\alpha]_D$ to be a mixture of a cholestanyl iodide (cf. the crude compound isolated above) and cholest-7-ene.

Amine oxide degradations

(a) *Oxidation with hydrogen peroxide.* 6α-Dimethylaminocholestane (0·16 g) in a mixture of chloroform (15 ml) and methanol (15 ml) was treated with H_2O_2aq (30%; 0·3 ml) and the mixture refluxed for 96 hr; excess of peroxide was then decomposed with Pt black catalyst, the mixture was filtered, and the filtrate was evaporated. The light-petroleum soluble residue was separated with HClaq into 6α-dimethylaminocholestane hydrochloride (80 mg) identified by mixed m.p. and IR spectrum and a neutral fraction, (68 mg) mainly cholest-6-ene, m.p. 56°; $[\alpha]_D$ −74°, ν_{max}^{KBr} 770 (strong), 797,830 cm⁻¹ (both very weak); m.p. after one recrystallization from alcohol 79–81. Physical properties of pure cholest-6-ene are quoted above; cholest-5-ene has m.p. 95°, $[\alpha]_D$ −56°, ν_{max} 797,832 cm⁻¹. The $[\alpha]_D$ of the crude hydrocarbon mixture is probably not in this case a good criterion of composition.

When 6β-, 7α- and 7β-dimethylaminocholestane (49 mg, 74 mg, and 52 mg respectively) were treated similarly to the 6α-isomer, the products were the recovered hydrochlorides (34 mg, 65 mg and 26 mg) and unidentified oils (10 mg, 20 mg and 25 mg respectively) having a variety of IR peaks in the carbonyl absorption region.

(b) *Oxidation with peracetic acid.* 6α-Dimethylaminocholestane (50 mg) in chloroform (5 ml) was treated with 38% peracetic acid in acetic acid (0·1 ml) and the mixture let stand at room temp for 48 hr, cooled to 0°, extracted with dil. NaOHaq, and evaporated. The residue (43 mg), which was completely soluble in light-petroleum and had ν_{max}^{film} 960; 3100 cm⁻¹, bands possibly attributable to an amine oxide,[19] was warmed to 60° for 10 min and then pyrolysed at 200–220°/0·02 mm. The product was nearly pure cholest-6-ene, m.p. 80–82°, $[\alpha]_D$ −84°, ν_{max}^{KBr} 770 (very strong), 797,830 cm (both very weak); m.p. after one recrystallization from alcohol 85–86° (Found: C, 87·5; H, 12·3. Calc. for $C_{27}H_{46}$: C, 87·5; H, 12·5%).

6β- and 7α-Dimethylaminocholestane (51 mg and 48 mg) treated with peracetic acid and the mixture then worked up under the same conditions as above gave light petroleum-soluble products in which no spectroscopic evidence for presence of amine oxides was detected, but which yielded, without pyrolysis, cholest-6-ene of quality exactly the same as that obtained above; this hydrocarbon

[19] A. A. Oswald and D. L. Guertin, *J. Org. Chem.* **28**, 651 (1963).

TABLE 1. PHYSICAL PROPERTIES AND ANALYSES FOR DERIVATIVES OF 7-AMINOCHOLESTANES

Systematic name ("new" compounds italicized)	m.p. (recryst. solvent in brackets)		$[\alpha]_D$		Analysis (this paper) Found (upper line) Calc. or reqd. (lower line)					Molecular formula
	this paper	lit. (ref. no.)	this paper	lit. (ref. no.)	C	H	N	Cl	I	
7α-Aminocholestane		15° (7)		−20° (7)						
7α-Aminocholestane hydrochloride	128–130°	141–143° (8)		−1° (8)	76·6 76·5	11·8 11·9	2·9 3·3	8·4 8·4		$C_{27}H_{50}NCl$
7α-Acetamidocholestane	204–206° (light pet.)	216–218° (7)	−14°	+40° (7)	81·4 81·0	12·3 12·0				$C_{29}H_{51}NO$
7α-Dimethylaminocholestane	83–84° (AcMe)		−34°		83·9 83·8	13·0 12·9	3·5 3·4			$C_{29}H_{53}N$
7α-Dimethylaminocholestane hydrochloride	256–259°d. (AcMe–CHCl₃)	280°d. (8)	−4°	−5° (8)			3·0 3·1	7·9 7·8		$C_{29}H_{54}NCl$
7α-Cholestanyltrimethylammonium iodide	199–201° (AcMe)		−6°		65·0 64·6	10·4 10·1	2·8 2·5		23·1 22·8	$C_{30}H_{56}NI$
7β-Aminocholestane		oil (7)		+40° (7)						
7β-Aminocholestane hydrochloride	290–292°d. (EtOAc–MeOH)	252–234° (sic; 7) 290°d. (8)	−49°	+50° (8)	76·5 76·5	11·6 11·9	3·2 3·3	8·5 8·4		$C_{27}H_{50}NCl$
7β-Acetamidocholestane	215° (light pet.)	148–150° (7)	+47°	+61° (7)	81·0 81·0	12·2 12·0				$C_{29}H_{51}NO$
7β-Dimethylaminocholestane	oil				83·7 83·8	12·7 12·9				$C_{29}H_{53}N$
7β-Dimethylaminocholestane hydrochloride	214–215° (EtOAc–CHCl₃)	211–213° (8)	+44°	+40° (8)				7·7 7·8		$C_{29}H_{54}NCl$

Table 2. Degradation of 7α-cholestanyltrimethylammonium iodide to mixtures of cholest-6-ene and cholest-7-ene

Weight of quaternary iodide taken, mg	Degradation conditions	Weight of hydrocarbon, mg	Weight of recovered base as hydrochloride mg	m.p. of hydrocarbon		$[\alpha]_D$ of hydrocarbon		Approximate % of cholest-7-ene in crude hydrocarbon
				crude	after 1 rextn. from EtOH	crude	after 1 rextn. from EtOH	
140	Refluxing 2N–KOH in EtOH (2 c.c.; 4 hr.)	86	9	60–65°	86°	−86°	−88°	2
40*	Refluxing EtOH (2 c.c.; 12 hr)	10	—	78–79°	86°	+12°	—	100
112	Pyrolysis[44] of quaternary hydroxide (made with Ag₂O)	72	4	50–60°	82–83°	−55°	−78°	33

* 25 mg undecomposed quaternary salt recovered using the method described[44] by Gent and McKenna in examination of the 6β-quaternary salt.

was the chief product in each case, but small amounts of the bases were also recovered as hydrochlorides (6β-, 2·6 mg; 7α-, 3·6 mg) identified by mixed m.p. and IR spectra. The cholest-6-ene was in each case identified by m.p., IR spectrum, and elemental analysis (for the once-recrystallized hydrocarbon from the 6β-oxide, found: C, 87·5; H, 12·7; from the 7α-oxide, found: C, 87·3; H, 12·7%).

7β-Dimethylaminocholestane (81 mg) similarly treated with peracetic acid, gave a product lacking the IR bands of an amine oxide. The product was separated with HClaq into 7β-dimethylaminocholestane [hydrochloride (66 mg) identified by mixed m.p. and IR spectrum] and an unidentified oil (16 mg) which may have contained a little cholest-6-ene (band at 770 cm^{-1}); the IR spectrum also exhibited bands at 1600 (weak) and 1550 cm^{-1} (very strong).