Synthesis, Structure, and Reactions of Secosteroids containing a Medium-sized Ring. Part 17.[1] Structure–Reactivity Relationship in the Solvolysis of 5,10-Secosteroidal 3-Tosylates [2]

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Kinetic measurements of the solvolysis of (*Z*)-3α- and (*Z*)-3β-, and (*E*)-3α- and (*E*)-3β-tosyloxy-5,10-secocholest-1(10)-en-5-ones in buffered aqueous acetone (90 : 10 v/v) reveal that the (*Z*)-3α-, (*E*)-3α-, and (*E*)-3β-tosylates are solvolysed according to a first-order rate law (the relative rates being *ca.* 1 : 3 : 8), while the (*Z*)-3β-ester, under the same conditions, reacts at a much slower rate by a complex mechanism, the kinetics of which are best approximated by a second-order law. These data and product analysis indicate that the former three esters are solvolysed with considerable double bond participation [resulting in the case of the (*E*)-3-esters in intramolecular cyclopropane ring closure], and that this interaction is unimportant for the (*Z*)-3β-tosylate. On the basis of conformational analysis of the starting tosylates and stereoelectronic requirements for homoallylic interaction, a possible mechanistic pathway for these solvolyses is proposed.

NUMEROUS studies of homoallylic interaction in various systems have been made in order to establish the nature of the reactive intermediates [3] and the necessary stereoelectronic requirements [4,5] leading to homoallylic participation. Of these, only a few relate to the stereochemical aspects of such interactions in medium-sized rings.[5-7] The present study, which is concerned with solvolyses of 5,10-secosteroidal 3-esters, comprises a full set of stereoisomers, both with respect to the configuration of the double bond and to the homoallylic chiral centre containing the leaving group in a ten-membered ring, *i.e.* (*Z*)-3α- and (*Z*)-3β-, and (*E*)-3α- and (*E*)-3β-tosyloxy-5,10-secocholest-1(10)-en-5-one [compounds (3c)—(6c)], and should thus provide valuable information on the configurational and conformational features affecting homoallylic participation in such systems.

RESULTS

Synthesis of Tosylates (3c—6c).—These compounds were prepared as shown in Scheme 1. Fission of the 5,10-bond in 5β-cholestane-3α,5-diol 3-acetate (1) [8] by photolytic lead tetra-acetate oxidation gave (*Z*)- and (*E*)-3α-acetoxy-5,10-secocholest-1(10)-en-5-one (3a) and (4a),[9] while a similar fission of 5α-cholestane-3β,5-diol 3-acetate (2) [10] by the lead tetra-acetate–iodine and mercuric oxide–iodine reaction afforded the (*Z*)- and (*E*)-3β-epimers (5a) and (6a),[11-13] respectively. From these acetates (3a)—(6a) the corresponding 3-tosylates (3c)—(6c) were prepared by mild alkaline hydrolysis and subsequent esterification of the resulting keto-alcohols (3b)—(6b) [9,11] with tosyl chloride in pyridine, in the usual way.[14]

Solvolysis of Tosylates (3c)—(6c).—Solvolysis of the stereoisomeric tosylates (3c)—(6c) was carried out in acetone–water (90 : 10 v/v) at 80 and 90° in the presence of one mol. equiv. of potassium acetate, by using the sealed ampoule technique. The solvolyses were followed up to at least 75—90% completion by potentiometric titration of unchanged potassium acetate with 0.018M aqueous hydrochloric acid. The rate constants for tosylates (3c), (4c), and (6c) were calculated from the standard first-order rate law, using a least-squares computer program. The rate constant for tosylate (5c) best obeyed the second-order rate law, but is less reliable. The rate constants and the derived enthalpy of activation and entropy of activation values are summarized in Table 1. These values are the average of two independent kinetic measurements.

TABLE 1

Solvolysis rates of stereoisomeric 3-tosyloxy-5,10-secocholest-1(10)-en-5-ones (3c)—(6c)

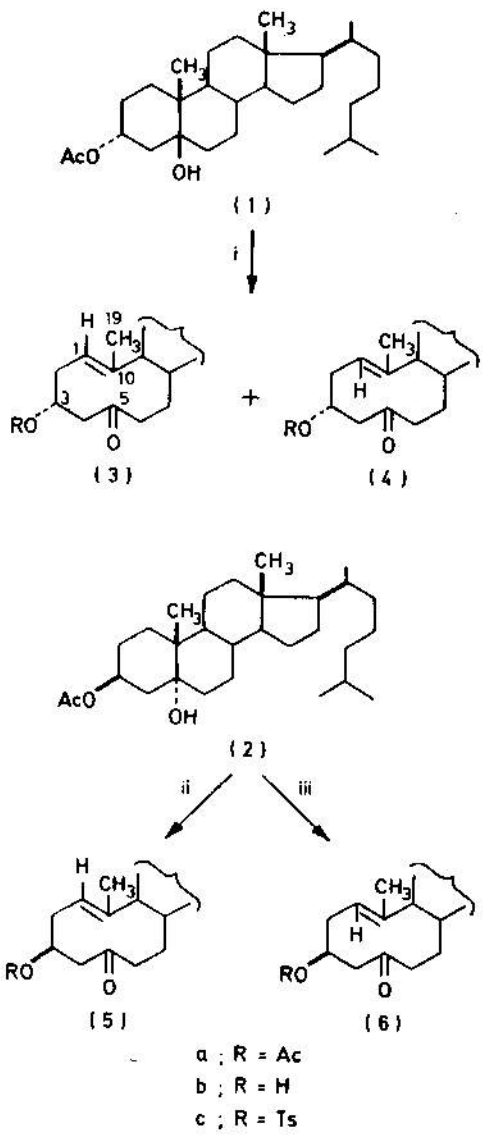
Tosylate	*T*/°C (±0.02)	k_1/s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
(3c)	80.00	$(1.22 \pm 0.02) \times 10^{-4}$	85.3 ± 3.7	76 ± 10
	90.00	$(2.83 \pm 0.03) \times 10^{-4}$		
(4c)	80.00	$(4.00 \pm 0.05) \times 10^{-4}$	82.8 ± 1.9	77 ± 5
	90.00	$(8.93 \pm 0.03) \times 10^{-4}$		
(6c)	80.00	$(1.07 \pm 0.01) \times 10^{-3}$	77.4 ± 2.7	84 ± 7
	90.00	$(2.26 \pm 0.02) \times 10^{-3}$		
		k_2/dm^3 mol^{-1} s^{-1}		
(5c)	80.00	$\sim 8 \times 10^{-7}$		
	90.00	$\sim 2 \times 10^{-6}$		

Large scale experiments for product analysis were carried out at 80° [for (3c), (4c), and (6c)] or 100° [for (5c)], under the same solvolytic conditions described above for rate determination. The products were isolated and separated by column chromatography on silica gel. The following comments can be made about the results obtained.

(i) The (*Z*)-3α-tosyl ester (3c) is solvolysed to give a mixture of two elimination products (Scheme 2), *i.e.* the

1(10),2- and 1(10),3-dien-5-ones (7) and (8) (in an overall yield of 4%),* *ca.* 91% of the hydroxy compound (3b) with unchanged configuration at C(3), and $<2\%$ of the epimeric alcohol (5b) with the 3β-configuration, indicating a high degree of stereoselectivity in the course of solvolysis.

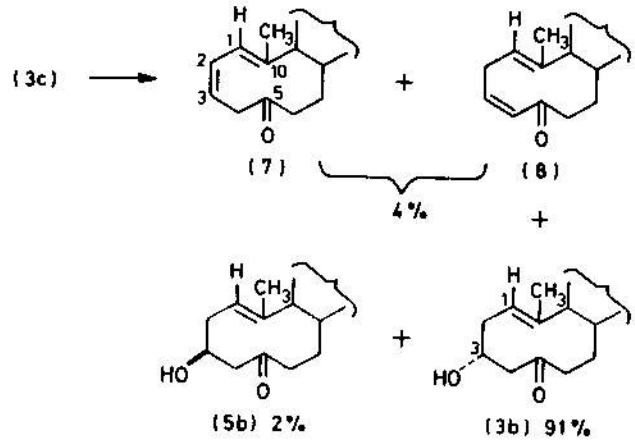
(ii) The (*Z*)-3β-tosylate (5c), under analogous reaction conditions, affords several products (Scheme 3), *i.e.* the same



Scheme 1 Reagents: i, $Pb(OAc)_4$–*hν*; ii, $Pb(OAc)_4$–I_2; iii, HgO–I_2

mixture of the two elimination products (7) and (8) formed in the solvolysis of the 3α-epimer (3c), but now in a substantially higher overall yield of 64%, a 1 : 4 mixture of the 3α-and the 3β-acetates (3a) and (5a) (in 20% yield), and a 1 : 1.5 mixture of the 3α- and 3β-alcohols (3b) and (5b) (in 7.5% yield).

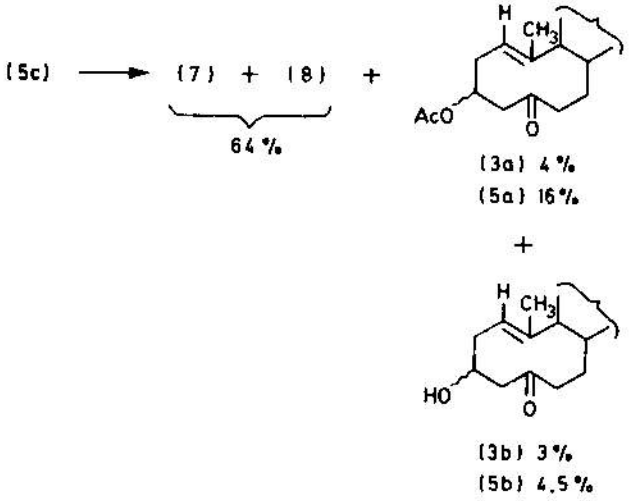
(iii) The solvolysis of the (*E*)-3α-tosylate (4c) proceeded mainly by intramolecular cyclopropane ring closure (Scheme 4) to give the 10-hydroxy-compound (9) in 64% yield. The (*E*)-3α-hydroxy-seco-ketone (4b) with unchanged configuration at C(3) is the only other product formed in this reaction (in 34% yield). When the cyclopropane derivative (9) was treated with mesyl chloride under alkaline conditions, it was converted into the corresponding 10,19-unsaturated cyclopropane product (10).



Scheme 2

(iv) Under the same solvolytic conditions, the (*E*)-3β-tosylate (6c) furnished products (11) and (12) (Scheme 5), in 1 and 32% yield respectively, which both contain a fused cyclopropane ring; † in addition, the acetate (6a) (35%) and alcohol (6b) (30%) were obtained, both with unchanged configuration at C(3). The hydroxy-cyclopropane derivative (11) could be readily dehydrated by means of mesyl chloride to give (12).

Since separate experiments have shown that all the products are stable under the solvolytic conditions used, the relative yields obtained upon isolation reflect the product



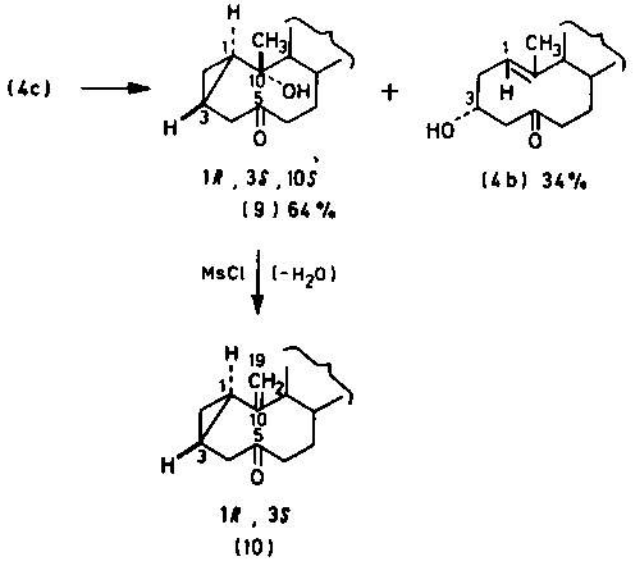
Scheme 3

distribution resulting from the original solvolyses. The constitution and stereochemistry of all subsititution products in Schemes 2—5 were established by direct comparison with authentic compounds (Scheme 1), while the

* Since products (7) and (8) could not be separated by column chromatography, they were identified by i.r., n.m.r., u.v., and mass spectra.

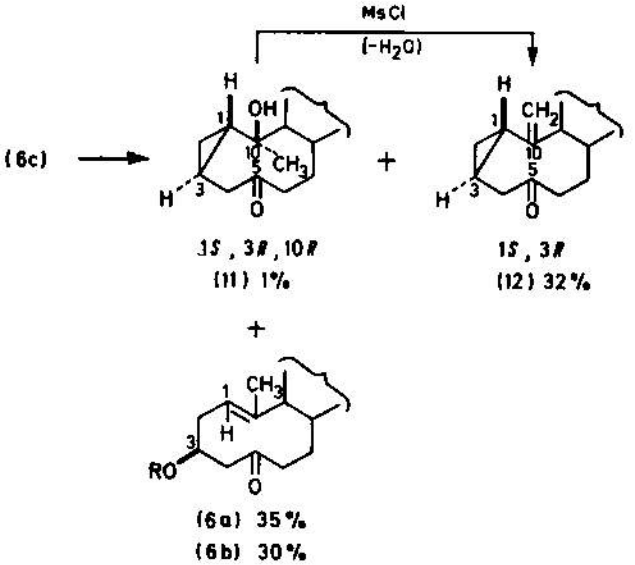
† It is noteworthy that when the (*E*)-3β-tosylate (6c) is refluxed for a long time in acetone containing $CH_3CO_2Na,3H_2O$, product (12) is formed in $>90\%$ yield.[14]

constitutions of the cyclopropane-ring-containing products (Schemes 4 and 5) were determined by elemental microanalysis, i.r., n.m.r., and mass spectra, and the chemical transformations outlined in Schemes 4—6.



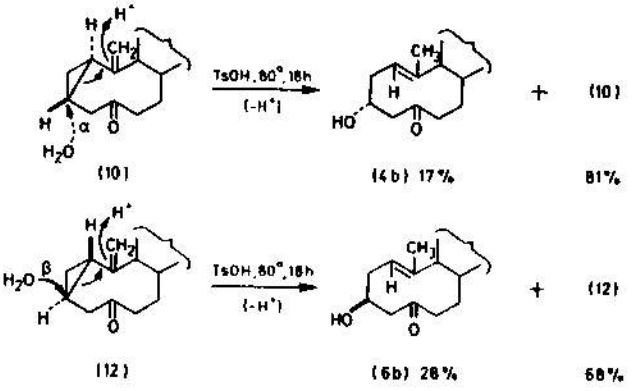
SCHEME 4

Configuration at C(1) *and* C(3) *in the Cyclopropane Ring-containing Products* (9)—(12).—From spectral and other characteristics it follows that the 10-hydroxy-cyclopropyl compound (9), derived from the (*E*)-3α-tosylate (4c), and its dehydration product (10) are configurationally different from the corresponding products (11) and (12) formed in the solvolysis of the (*E*)-3β-tosylate (6c). Since the bicyclo-[7.1.0] system can be either *cis*- or *trans*-fused, the observed difference may arise from stereoisomerism at the C(1) and/or



SCHEME 5

C(3) ring-junction atoms. However, the mechanism of intramolecular cyclopropane ring formation in this type of reaction [7] implies that displacement of the leaving 3-tosyloxy group (as anion) by the π-electron pair of the 1,10 double bond should occur from the backside, *i.e.* with inversion of configuration at C(3). Consequently, the configuration at C(3) in the cyclopropane-ring-containing compounds (9) and (10) should be opposite to that in products (11) and (12) (and predictable in both series). This assumption was supported by stereospecific acid-catalysed opening of the cyclopropane ring system in compounds (10) and (12),* which resulted in the formation (Scheme 6) of (*E*)-3α- and (*E*)-3β-hydroxy-5,10-secocholest-1(10)-en-5-one (4b) and (6b), respectively, again with inversion of configuration at C(3). Therefore, the 10-hydroxy-cyclopropyl compound (9), obtained from the (*E*)-3α-tosyl ester (4c), and its derivative (10) should have the 3*S* configuration, while products (11) and (12), formed in the solvolysis of the (*E*)-3β-tosylate (6c), the 3*R* configuration. In order to obtain firm evidence on the stereochemistry (*cis* or *trans*) of the fused bicyclo[7.1.0] ring system and the configuration (*R* or *S*) of the ring-junction atoms in the cyclopropane products (9)—(12),



SCHEME 6

particularly of C(1), the stereoisomeric 10,19-unsaturated 5-ketones (10) and (12) and the 10-hydroxy-cyclopropyl product (9) were subjected to *X*-ray crystallographic analysis,[15] which showed, unequivocally, that compounds (9) and (10) have the *trans*-1*R*,3*S* configuration, and product (12) [and therefore also the minor 10-hydroxy-cyclopropyl derivative (11)] the *trans*-1*S*,3*R* configuration. Moreover, for alcohol (9) the configuration at C(10) was found to be 10*S*,[16] while for the stereoisomeric alcohol (11) it should be 10*R*, if one assumes, reasonably, addition of water to C(10) from the outside of the ten-membered ring in the reactive carbocation intermediate with a B_3 conformation [see (6c and e) in Scheme 7].

DISCUSSION

Results of both rate measurements (Table 1) and product analysis (Schemes 2—5) point to some characteristic differences in the solvolytic reactivity of the four diastereoisomeric tosylates (3c)—(6c). Thus, while the esters (3c), (4c), and (6c) are solvolysed according to a first-order rate law (the relative rates being *ca.* 1 : 3 : 8), the (*Z*)-3β-tosylate (5c), under the same conditions,

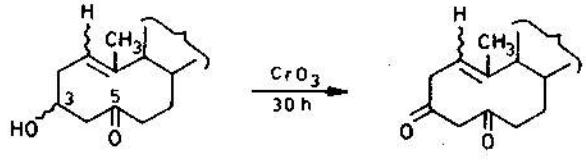
* Ring-opening of both unsaturated cyclopropane derivatives (10) and (12) was performed under the conditions used for solvolysis but with a 20—30% excess of toluene-*p*-sulphonic acid, *i.e.* in acetone–water (90 : 10 v/v) in the presence of 1 mol equiv. of potassium acetate and 1.2—1.3 mol equiv. of toluene-*p*-sulphonic acid at 80°. When only 1 mol equiv. (or less) of acid was used, both compounds (10) and (12) remained unchanged, even after prolonged heating.

reacts at a much slower rate by a complex mechanism, the kinetics of which are best approximated by a second-order rate law. Moreover, when subjected to solvolysis, the former three tosylates (3c), (4c), and (6c) afford substitution products with exclusive or almost exclusive retention of configuration at C(3), the (*E*)-esters (4c) and (6c) also undergoing internal cyclopropane ring closure, whereas tosylate (5c) behaves differently and, besides a considerable amount of elimination products, furnishes substitution products with both retention and inversion of configuration at C(3).

It seems unlikely that these differences in reactivity between tosylates (3c), (4c), and (6c), on the one hand, and the (*Z*)-3β-ester (5c), on the other, can be ascribed to ground state energy differences.* This is substantiated by the results of semi-quantitative rate determinations of the oxidation of the corresponding stereoisomeric 3-alcohols (3b)—(6b) with chromic anhydride (Table 2),

TABLE 2

Oxidation of the stereoisomeric 3-hydroxy-5,10-secocholest-1(10)-en-5-ones (3b)—(6b) with chromic anhydride



Alcohol	Ketone	Yield %	Relative rate
(3b)	*Z*	54	1.2
(4b)	*E*	46	1
(5b)	*Z*	68	1.5
(6b)	*E*	74	1.6

which show that, under the same reaction conditions, the rates of oxidative conversion for all four alcohols differ to a much smaller extent than the solvolytic rates of the corresponding tosylates, particularly when the *Z*–*E* diastereoisomeric alcohols with the same configuration at C(3) are compared. Since in unsubstituted 4- to 14-membered cyclic systems parallelism between oxidation and solvolytic processes has been observed,[17] one might expect, in the absence of other effects, similar results for the solvolytic reactivity of the corresponding tosylates (3c)—(6c) (which, however, is not the case).

These findings indicate that the spatial relationship of the 1,10 double bond to the reaction centre at C(3) in the ten-membered ring is one of the major factors which determines the solvolytic reactivity of the stereoisomeric tosylates (3c)—(6c), namely that the esters (3c), (4c), and (6c) are solvolysed *with* homoallylic double bond participation and that this interaction is *unimportant* in the solvolysis of the (*Z*)-3β-tosylate (5c). However, the relative reactivities of the tosylates (3c), (4c), and (6c) cannot be fully explained only on the basis of different degree of homoallylic assistance, the rate factors of 1 : 3 : 8 being too small to be significant, particularly when compared with the product distribution. Of these three esters (3c), (4c), and (6c) only the *E*-isomeric tosylates (4c) and (6c) undergo solvolysis with cyclopropane ring formation (Schemes 4 and 5), indicating more pronounced homoallylic participation in the *E*-series; however, the slower reacting of the two *E*-tosylates, *i.e.* the 3α-epimer (4c) affords more cyclopropane derivative [64% (9)] than the faster reacting 3β-epimer (6c) [33% (11) + (12)]. In addition, the only cyclopropane ring-containing compound (9) produced from the 3α-tosylate (4c), and the predominant cyclopropane derivative (12) formed from the 3β-epimeric ester (6c), are structurally different at C(10) (which means that the energy profile of the two solvolyses should not necessarily be the same), and have opposite configurations at the ring junction atoms C(1) and C(3) [15] (Schemes 4 and 5). The extent of homoallylic assistance in the course of solvolysis is also insufficient to account for the fact that the stereoisomeric (*Z*)- and (*E*)-3α-tosylates (3c) and (4c) undergo substitution with alcohol formation only (Schemes 2 and 4), while the (*Z*)- and (*E*)-3β-esters (5c) and (6c) afford as substitution products both the acetates and alcohols (Schemes 3 and 5). In order to rationalize all these results, it is necessary to consider the spatial factor (extent of homoallylic assistance) in combination with the conformational factor, *i.e.* the ease of adoption by the ten-membered ring of the conformation(s) suitable for homoallylic participation, the orientation between the 1,10 double bond and the reaction centre at C(3) in these conformations, the stability of the intermediate homoallylic carbonium ion(s), steric interactions in the transition state, *etc.*

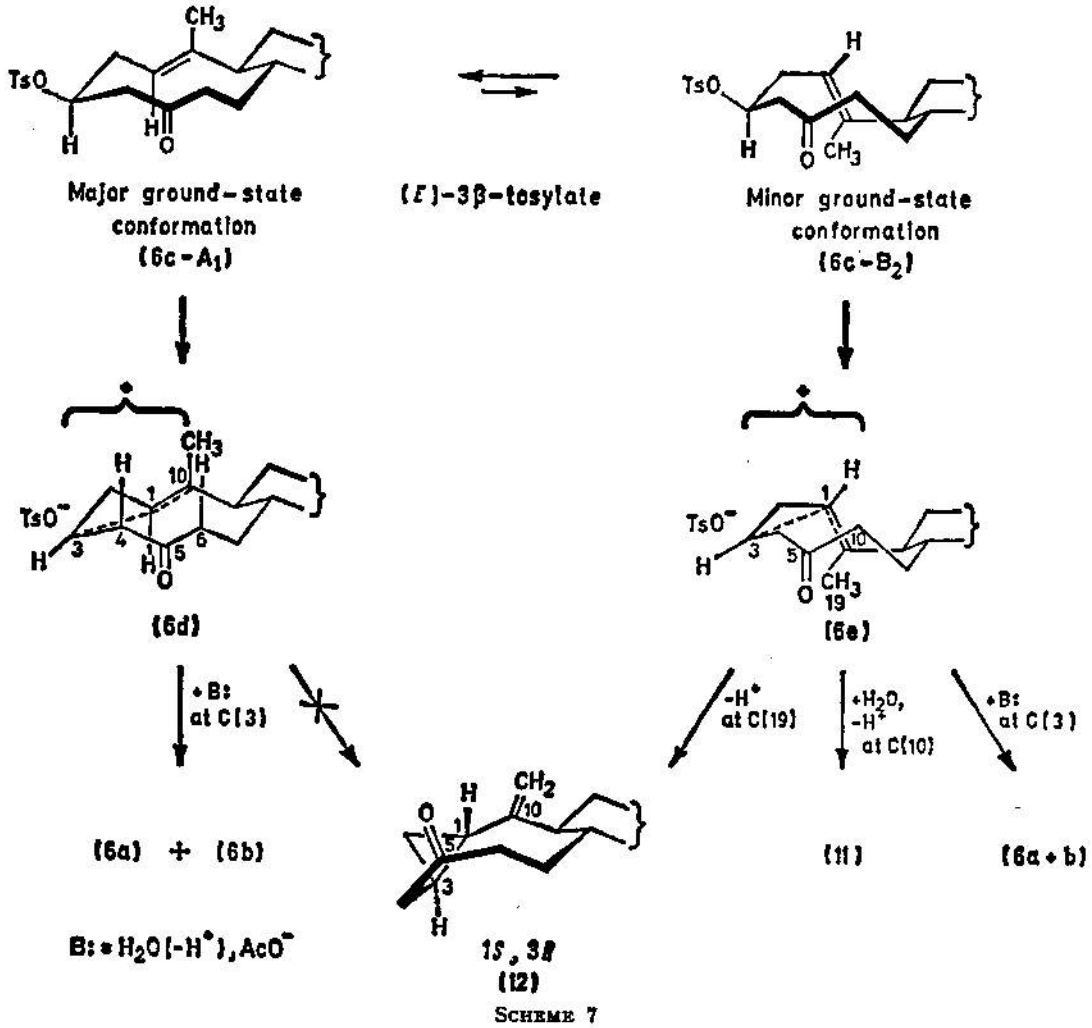
Inspection of Dreiding models reveals that the 1,10 double bond of the *E*-esters (4c) and (6c) can change its relative spatial orientation and thus approach the reaction centre at C(3) in two conformationally different ways, both able to assist ionization of the leaving group. For the (*E*)-3β-tosylate (6c) such spatial arrangements of the reaction sites are present in the most stable ground state conformation [(6c-A_1), Scheme 7] and in the less stable (minor) conformation [(6c-B_2), Scheme 7]†,[18] Therefore, from the models, it seems possible that the solvolysis of ester (6c) can take place by the intermediacy of at least two conformationally different homoallylic carbonium ions (6d and e), mutually distinguishable only when C(1) is involved in σ-bond formation. Thus, both carbonium ions (6d and e) can undergo stereospecific addition of a nucleophilic species (AcO^-, H_2O) at C(3) to afford the 3β-substitution products (6a and b), but only carbonium ion (6e) can also form intra-

* *Although the unsubstituted Z-cyclodecene ring is ca. 13.8 kJ mol⁻¹ more stable than the corresponding E-ring,*[16] *incorporation of one sp^2 hybridized (carbonyl) carbon at C(5) in the unsaturated ten-membered ring of 5,10-secosteroid molecules and the presence of other substituents in these compounds, including the steroid rings C and D, should cause a lowering of this ground state energy difference.*

† The preferred (major and minor) conformations in solution of all the esters studied in the present work were inferred [actually for the acetates (3a)—(6a)] from ^1H and ^{13}C n.m.r. spectral data [(6a),[18] (4a),[9] (3a), and (5a) [19]].

molecularly a *trans* C(1)–C(3) bond, either with water addition at C(10) [to give (11)] or proton elimination at C(19) [to give (12)]. Therefore, from the product distribution (the ratio of cyclisation to 3β-substitution products being *ca.* 1 : 2, Scheme 5), it is evident that at least one third of the ester molecules reacts in the less stable (minor) conformation B_2 [*i.e. via* (6e)], although the conformational models it can be anticipated that the homoallylic cation(s) (6d and/or e) are relatively stable, and therefore live long enough to encounter at C(3) not only water [resulting in 30% (6b)], but also the more nucleophilic, albeit less concentrated, acetate ion,* and thus give 35% of the (*E*)-3β-acetate (6a).

On similar considerations, *i.e.* on the basis of (ground

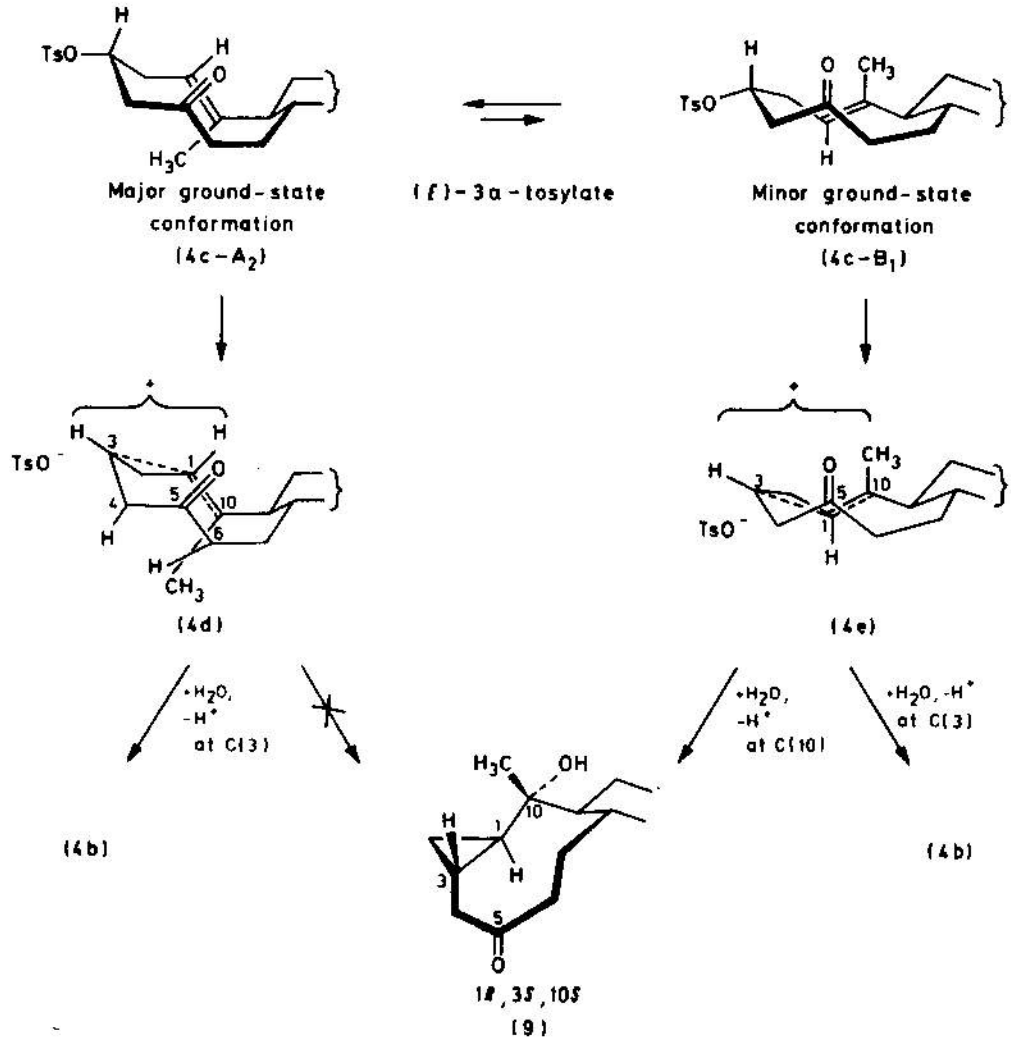


SCHEME 7

participation of either conformation A_1 (6d) or B_2 (6e) in substitution reactions is possible and cannot be excluded on the basis of the present evidence. Probably 1,3-cyclisation of the 3β-ester by way of (6d), corresponding to the most stable ground state conformation A_1, which would lead to a *cis*-bicyclo[7.1.0] ring system with α-hydrogens at C(1) and C(3), involves considerable steric compression due to repulsion between the 10-CH_3 group and the ' axial ' transannular β-hydrogens at C(4) and/or C(6), and therefore such a *cis*-cyclopropane product is not formed. Steric reasons can also be invoked to explain the fact that water addition at C(10) in the carbonium ion (6e) is energetically unfavourable and takes place only to a minor extent (*ca.* 1%), compared with the amount of elimination at C(19) [32% (12)]. From state) conformations deduced for the ten-membered ring of the (*E*)-3α-ester [(4c), Scheme 8] [9] and product analysis (Scheme 4), one can conclude that at least two-thirds of the (*E*)-3α-tosylate must undergo ionization at C(3) with assistance by the double bond in the less stable (minor) conformation [(4c-B_1), Scheme 8], to give the homoallylic carbonium ion (4e). On the other hand, the preferred (most stable) ground state conformation [(4c-A_2), Scheme 8] [9] of this 3α-ester would produce the conformationally different homoallylic carbonium ion [(4d), Scheme 8]. Both ions (4d and/or e), which are different from, and apparently less stable than, the carbocations

* Under the conditions used in this study, the molar ratio tosylate : AcOK:H_2O at the beginning of the reaction was *ca.* 1 : 1 : 300.

(6d and/or e) [generated from the (*E*)-3β-tosylate (6c)], collapse in a fast reaction with the surrounding water (but not acetate ion) to furnish the (*E*)-3α-hydroxy-seco-ketone (4b), whereas only the carbonium ion (4e), in a conformation corresponding to B_1, undergoes intramolecular C(1)–C(3) bond formation and water addition to C(10), to give the *trans*-10-hydroxy-cyclopropyl product (9) (Scheme 8).* The formation of the latter, hydroxylated compound (9) in 64% yield indicates that nucleophilic attack by water (from the outside of the ten-membered ring) at the preferred tertiary C(10) carbonium ion site in the homoallylic cation (4e) is not associated with significant steric strain in the transition state.



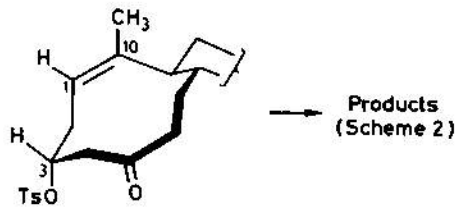
Scheme 8

In this way, the solvolytic reactivity and behaviour of the (*E*)-3α- and (*E*)-3β-tosylate esters (4c) and (6c) (including the formation and stereochemistry of the solvolysis products) can be satisfactorily interpreted.

The difference in solvolytic reactivity is even more pronounced in the 3-epimeric (*Z*)-tosylates (3c) and (5c) (Table 1, Schemes 2 and 3). Since in the stable conformation(s) of both esters (Schemes 9 and 10) [19] the spatial orientation of the 1,10 double bond cannot be changed without a very strong increase in *I* strain, the possibility of homoallylic participation will depend only on the relative position of the 3-tosyloxy-group. In the (*Z*)-3α-epimeric tosylate (3c) (Scheme 9) the steric relationship between the double bond and the leaving group at C(3) is favourable for assisted ionization; however, this interaction is not strong enough to permit C(1)–C(3) bond formation, and therefore the resulting homoallylic carbonium ion undergoes a predominantly stereospecific reaction at C(3) with water to give the (*Z*)-3α-hydroxy-seco-ketone (3b), with retention of configuration at C(3) (Scheme 2).

* Probably, in this case also, repulsive interactions between the 10-CH_3 group and transannular ' axial ' α-hydrogens at C(4) and/or C(6) in carbonium ion (4d), derived from conformation A_2, from which a *cis*-bicyclo[7.1.0]ring system with β-hydrogens at C(1) and C(3) could be expected, are strong enough to prevent internal 1,3-bond formation.

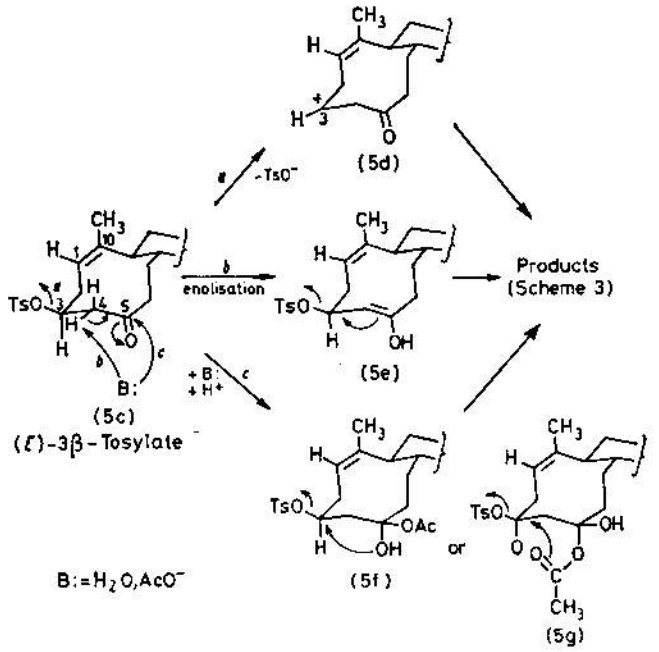
In the (*Z*)-3β-tosylate (5c) (Scheme 10) homallylic assistance to ionization at C(3) by the π-electrons of the 1,10 double bond is not possible (for stereoelectronic reasons), and therefore this epimeric ester is solvolysed without homoallylic interaction (Scheme 3). Moreover,



(3c)
(*Z*)-3α-Tosylate

SCHEME 9

it appears that in the absence of homoallylic participation, 'normal' solvolysis of the (*Z*)-3β-tosylate (5c), *via* ion (5d), is largely suppressed (Scheme 10, path *a*) and that reaction at C(3) proceeds to a considerable extent under the influence of the 5-oxo-group. Thus, one may reasonably assume that the first, rate-determining step of this reaction of (5c) involves base-catalysed abstraction of hydrogen adjacent to the oxo-group, with subsequent enolisation to (5c) and allylic participation (Scheme 10, path *b*),[20] or nucleophilic attack at the 5-oxo-carbonyl carbon with formation of an intermediate adduct (5f or



SCHEME 10

g), which could undergo 1,4-hydroxy oxygen or 1,6-carbonyl oxygen participation, respectively (Scheme 10, path *c*).* The existence of these reactive intermediates [(5d-g), Scheme 10] would account for the substantial amount of elimination products (7) and (8) obtained and for nonstereospecific substitution at C(3) with formation of the epimeric 3-alcohols (3b) and (5b) and the corresponding 3-acetates (3a) and (5a) (Scheme 3).

This study has shown that the solvolytic behaviour of (*Z*)- and (*E*)-3-tosyloxy-5,10-secocholest-1(10)-en-5-ones (3c)—(6c) is highly dependent on the stereoelectronic conditions for an effective homoallylic π-bond overlap with the incipient (empty) *p*-orbital at the C(3) reaction centre, in the rate-determining step. For the (*Z*)-3-tosylates (3c) and (5c), owing to the relative immobility of the *Z*-double bond, these conditions should be fulfilled in the ground state (or some similar) conformations [as in the case of the (*Z*)-3α-tosylate (3c)]. On the other hand, this is not so for the (*E*)-tosylates (4c) and (6c); since in these compounds the *E*-double bond is relatively flexible, it can change its spatial orientation in order to meet stereoelectronic requirements for effective homoallylic participation, with the consequence that the *E*-esters can react preferentially [*e.g.* the 3α-tosylate (4c)] or at least partially [*e.g.* the 3β-tosylate (6c)] in their respective less stable conformations. This indicates that the Curtin–Hammett principle can be applied to the solvolysis of the (*E*)-3-tosylates (4c) and (6c).

EXPERIMENTAL

M.p.s are uncorrected. Optical rotations were measured in chloroform. N.m.r. spectra were obtained at 100 MHz with a Varian HA-100 spectrometer in deuteriochloroform with tetramethylsilane as internal reference (chemical shifts are reported as δ values). I.r. spectra were determined on a Perkin-Elmer instrument, model 337. Mass spectra were taken on an Atlas CH5 mass spectrometer. Silica gel (0.05—0.2 mm) was used for preparative column chromatography. The separation of products was monitored by t.l.c., which was carried out on silica gel G (Stahl) with benzene–ethyl acetate (9 : 1 or 7 : 3), detection being effected with 50% aqueous sulphuric acid. Light petroleum refers to the fraction of b.p. 40—60 °C.

(*Z*)-3α-Hydroxy-5,10-secocholest-1(10)-en-5-one (3b) [9] had m.p. 116° (from acetone); $[\alpha]_D^{20}$ −14° (*c* 0.80); $\nu_{max.}$ (KBr) 3 498, 3 440, and 1 680 cm^{-1} (Found: C, 80.6; H, 11.6. Calc. for $C_{27}H_{46}O_2$: C, 80.5; H, 11.5%). (*E*)-3α-Hydroxy-5,10-secocholest-1(10)-en-5-one (4b) [9] was a glass, $[\alpha]_D^{20}$ −30° (*c* 0.55); $\nu_{max.}$ (CCl_4) 3 620, 3 470, 1 702, and 1 692 cm^{-1} (Found: C, 80.2; H, 11.3%). (*Z*)-3β-Hydroxy-5,10-secocholest-1(10)-en-5-one (5b) [11] had m.p. 118° (from methanol); $[\alpha]_D^{23}$ +38° (*c* 0.49); $\nu_{max.}$ (KBr) 3 279 and 1 695 cm^{-1} (Found: C, 80.4; H, 11.6%). (*E*)-3β-Hydroxy-5,10-secocholest-1(10)-en-5-one (6b) [11] had m.p. 158° (from methanol); $[\alpha]_D^{23}$ +27° (*c* 0.38); $\nu_{max.}$ (KBr) 3 448 and 1 698 cm^{-1} (Found: C, 80.8; H, 11.6%).

Synthesis of the 3-Tosylates (3c)—(6c).[14]—To a solution of the alcohol (3b)—(6b) (1 g) in anhydrous pyridine (15 ml), toluene-*p*-sulphonyl chloride (1.2 g) was added. The reaction mixture was kept at room temperature until the substrate was consumed (*ca.* 48 h) and was then poured into ice–water (*ca.* 100 ml) containing copper(II) sulphate (40 g) and extracted with ether. The ethereal layer was washed successively with water, aqueous sodium hydrogencarbonate, and water, dried ($MgSO_4$), and evaporated *in vacuo*. The

* At this time no attempts were made to distinguish between the two possible mechanisms (Scheme 10, path *b* or *c*), both of which would account for the kinetics of, and product formation in, the solvolysis of ester (5c).

residue was recrystallised from acetone to give the corresponding tosylate (yields 80—90%).

(Z)-3α-*Tosyloxy*-5,10-*secocholest*-1(10)-*en*-5-*one* (3c) had m.p. 119—120°; $[\alpha]_D^{20}$ +12° (*c* 1.35); $\nu_{max.}$ (KBr) 1 705, 1 590, 1 185, and 1 168 cm^{-1}; δ 0.67 (3 H, s, 13-Me), 0.85 (6 H, d, 25-Me_2), 0.89 (3 H, d, 20-Me), 1.59 (3 H, d, 10-Me), 2.42 (3 H, s, aryl Me), 4.72 (1 H, m, 3-H), 4.94 (1 H, m, 1-H), and 7.54 (4 H, q, aryl H) (Found: C, 73.1; H, 9.5. $C_{34}H_{52}O_4S$ requires 73.3; H, 9.4%). (E)-3α-*Tosyloxy*-5,10-*secocholest*-1(10)-*en*-5-*one* (4c) had m.p. 134°; $\nu_{max.}$ (KBr) 1 705, 1 610, 1 193, and 1 182 cm^{-1}; δ 0.68 (3 H, s, 13-Me), 0.84 (6 H, d, 25-Me_2), 0.87 (3 H, d, 20-Me), 1.78 (3 H, d, 10-Me), 2.48 (3 H, s, aryl Me), 4.80 (1 H, m, 1-H), 4.95 (1 H, m, 3-H), and 7.68 (4 H, q, aryl H) (Found: C, 73.2; H, 9.2%). (Z)-3β-*Tosyloxy*-5,10-*secocholest*-1(10)-*en*-5-*one* (5c) had m.p. 107°; $[\alpha]_D^{20}$ +34° (*c* 0.53); $\nu_{max.}$ (KBr) 1 705, 1 693, 1 193, and 1 182 cm^{-1}; δ 0.68 (3 H, s, 13-Me), 0.82 (6 H, d, 25-Me_2), 0.86 (3 H, d, 20-Me), 1.68 (3 H, d, 10-Me), 2.48 (3 H, s, aryl Me), 5.05 (1 H, m, 3-H), 5.20 (1 H, m, 1-H), and 7.60 (4 H, q, aryl H) (Found: C, 73.2; H, 9.5%). (*E*)-3β-Tosyloxy-5,10-secocholest-1(10)-en-5-one (6c) [14] had m.p. 140°; $[\alpha]_D^{20}$ +2° (*c* 0.53); $\nu_{max.}$ (KBr) 1 704, 1 692, 1 598, 1 194, and 1 180 cm^{-1}; δ 0.68 (3 H, s, 13-Me), 0.84 (6 H, d, 25-Me_2), 0.88 (3 H, d, 20-Me), 1.70 (3 H, d, 10-Me), 2.52 (3 H, s, aryl Me), 4.65 (1 H, m, 1-H), 5.0 (1 H, m, 3-H), and 7.62 (4 H, q, aryl H) (Found: C, 73.2; H, 9.5%).

Solvolysis of the 3-*Tosylates* (3c)—(6c).—*Kinetics.* Acetone was purified by boiling it with a small quantity of potassium permanganate, drying ($CaSO_4$), and distillation at atmospheric pressure. Water used in the kinetic studies was doubly distilled.

An accurately weighed amount of the 3-tosylate was dissolved in a measured volume of 90% aqueous acetone to give a 0.02M solution and 1 mol. equiv. potassium acetate was added. Portions (5.0 ml) were sealed off in glass ampoules and placed in a constant temperature (±0.02°) bath for appropriate periods. On removal from the thermostat, the ampoules were chilled in ice–water and the contents analysed by potentiometric titration of unconsumed potassium acetate with 0.018M hydrochloric acid, using a Radiometer 22 pH meter. Solvolyses of the esters (3c), (4c), and (6c) were followed up to about four half-lives, and that of the ester (5c) up to *ca.* 75% completion. The rate constants, shown in Table 1, were calculated in the usual manner and represent the average values of two separate experiments.

Products.—The esters (3c)—(6c) were solvolysed in buffered acetone–water (9 : 1 v/v) as described above. The reaction mixtures were worked up in the usual way and the components were separated by column chromatography.

Solvolysis of (Z)-3α-*Tosyloxy*-5,10-*secocholest*-1(10)-*en*-5-*one* (3c).—Tosylate (3c) (860 mg) was solvolysed at 80° for 8 h and the product was chromatographed on silica gel (24 g). Light petroleum–benzene (45 : 35) eluted a mixture of the unsaturated products (7) and (8) (24 mg, 4%) as an oil, M^+ 384; $\lambda_{max.}$ (EtOH) 229 nm; $\nu_{max.}$ (CCl_4) 1 698 (unconjugated carbonyl), 1 680 (conjugated carbonyl), and 1 640 cm^{-1} (conjugated double bond); δ 0.68 (3 H, s, 13-Me), 0.86 (6 H, d, 25-Me_2), 0.89 (3 H, d, 20-Me), 1.65 and 1.67 (3 H, d, 10-Me), *ca.* 2.65 (1 H, m, 2- and 4-H, respectively), *ca.* 3.70 (1 H, unstructured q, 2-H and 4-H, respectively), and 5.00—6.40 (3 H, m, 1- and 3-H, and partially 2- and 4-H, respectively). Elution with benzene–light petroleum (55 : 25) afforded the starting tosylate (3c) (16 mg, 2%). Benzene–ether (4 : 1) gave (*Z*)-3α-hydroxy-5,10-secocholest-1(10)-en-5-one (3b) (566 mg, 91%), m.p. 116° (from acetone) (i.r. and n.m.r. spectra identical with those of an authentic sample). Benzene–ether (3 : 1) afforded (*Z*)-3β-hydroxy-5,10-secocholest-1(10)-en-5-one (5b) (12 mg, 2%), m.p. 116—118° [i.r. spectrum identical with that of authentic (5b)].

Solvolysis of (Z)-3β-*Tosyloxy*-5,10-*secocholest*-1(10)-*en*-5-*one* (5c).—Tosylate (5c) (900 mg) was solvolysed at 100° for 12 days (288 h) * and the product was chromatographed on a column of silica gel (28 g). Light petroleum–benzene (45 : 35) eluted a mixture of the unsaturated products (7) and (8) (398 mg, 64%). Elution with benzene–light petroleum (55 : 25) gave starting material (5c) (76 mg, 8.5%). Benzene eluted (*Z*)-3β-acetoxy-5,10-secocholest-1(10)-en-5-one (5a) (116 mg, 16%), m.p. 138° (from acetone–methanol) (lit.,[11] 138°). Elution with benzene–ether (99 : 1) gave (Z)-3α-*acetoxy*-5,10-*secocholest*-1(10)-*en*-5-*one* (3a) (30 mg, 4%), identical with the compound obtained by acetylation of the (*Z*)-3α-hydroxy-derivative (3b), m.p. 129—130° (from acetone–methanol); $[\alpha]_D^{20}$ +17° (*c* 1.00); $\nu_{max.}$ (KBr) 1 728, 1 705, and 1 270 cm^{-1}; δ 0.68 (3 H, s, 13-Me), 0.87 (6 H, d, 25-Me_2), 0.91 (3 H, d, 20-Me), 1.64 (3 H, d, 10-Me), 2.06 (3 H, s, OAc), 4.90 (1 H, m, 3-H), and 5.10 (1 H, m, 1-H) (Found: C, 78.2; H, 10.8. $C_{29}H_{46}O_3$ requires C, 78.3; H, 10.9%). Benzene–ether (9 : 1) afforded (*Z*)-3α-hydroxy-5,10-secocholest-1(10)-en-5-one (3b) (19 mg, 3%) m.p. 116° (undepressed by admixture with an authentic sample). Elution with benzene–ether (4 : 1) gave (*Z*)-3β-hydroxy-5,10-secocholest-1(10)-en-5-one (5b) (30 mg, 4.5%), m.p. 118° (from methanol) (lit.,[11] 116—118°).

Solvolysis of (E)-3α-*Tosyloxy*-5,10-*secocholest*-1(10)-*en*-5-*one* (4c).—Tosylate (4c) (1.0 g) was solvolysed at 80° for 3 h and the mixture was worked-up in the usual way. The solid obtained after evaporation of solvent was recrystallised twice from acetone–methanol to give (1R,3S,10S)-10-*hydroxy*-1,3-*cyclo*-5,10-*secocholestan*-5-*one* (9) (405 mg, 56%), m.p. 174°; $[\alpha]_D^{20}$ −21° (*c* 0.97); $\nu_{max.}$ (KBr) 3 440, 3 080, and 1 704 cm^{-1}; δ 0.2—0.6 (2 cyclopropyl H, m), 0.69 (3 H, s, 13-Me), 0.80—0.90 (9 H, d, 25-Me_2 and s, 10-Me) (Found: C, 80.4; H, 11.7. $C_{27}H_{46}O_2$ requires C, 80.5; H, 11.9%). The mother-liquor was evaporated to dryness *in vacuo* and the residue (320 mg) treated with acetic anhydride (2.5 ml) and pyridine (2.5 ml) overnight at room temperature. It was then worked-up in the usual way to give a mixture (340 mg) which was chromatographed on silica gel (15 g). Benzene–ether (99 : 1) eluted (*E*)-3α-acetoxy-5,10-secocholest-1(10)-en-5-one (4a) [271 mg, 34%, based on the starting ester (4c)], m.p. 102° (from acetone) (lit.,[9] 102°). Elution with benzene–ether (9 : 1) afforded (1*R*,3*S*,10*S*)-10-hydroxy-1,3-cyclo-5,10-secocholestan-5-one (9) (58 mg, 8%), m.p. 174° (from acetone–methanol) [total yield of (9) 64%].

Solvolysis of (E)-3β-*Tosyloxy*-5,10-*secocholest*-1(10)-*en*-5-*one* (6c).—Tosylate (6c) (1.5 g) was solvolysed at 80° for 1.5 h. Elution with light petroleum–benzene (1 : 1) gave (1S,3R)-1,3-*cyclo*-5,10-*secocholest*-10(19)-*en*-5-*one* (12) (332 mg, 32%),[14] m.p. 103° (from acetone); $[\alpha]_D^{20}$ +58° (*c* 0.54); $\nu_{max.}$ (CCl_4) 3 080,1 700, and 1 638 cm^{-1}; δ 0.5—0.6 (2 cycloproyl H, m), 0.68 (3 H, s, 13-Me), 0.86 (6 H, d, 25-Me_2), 0.89 (3 H, d, 20-Me), and 4.49 and 4.59 (each 1 H, CH_2=C) (Found: C, 84.2; H, 11.6. $C_{27}H_{44}O$ requires C, 84.3; H, 11.5%). Benzene–ether (99 : 1) eluted (*E*)-3β-

* Preliminary experiments have shown that approximately the same proportions of the solvolysis products are obtained when the reaction is performed at 90°.

acetoxy-5,10-secocholest-1(10)-en-5-one (6a) (420 mg, 35%), m.p. 136° (from acetone–methanol) (lit.,[11,12] m.p. 136°). Elution with benzene–ether (8 : 2) afforded a mixture of two products indistinguishable on t.l.c., *i.e.* (1*S*,3*R*,10*R*)-10-hydroxy-1,3-cyclo-5,10-secocholestan-5-one (11) and (*E*)-3β-hydroxy-5,10-secocholest-1(10)-en-5-one (6b). This mixture was treated with acetic anhydride (3 ml)–pyridine (3 ml), kept at room temperature overnight, and worked-up in the usual way. The residue (400 mg) was chromatographed on silica gel (20 g). Benzene–ether (98 : 2) eluted (*E*)-3β-acetoxy-5,10-secocholest-1(10)-en-5-one (6a) [358 mg, 30% based on the starting ester (6c)], m.p. 136° (from acetone–methanol) (lit.,[11,12] 136°). Elution with benzene–ether (8 : 2) gave (1S,3R,10R)-10-*hydroxy*-1,3-*cyclo*-5,10-*secocholestan*-5-*one* (11) (12 mg, 1.1%), m.p. 104° (from acetone–methanol); $\nu_{max.}$ (CCl_4) 3 620, 3 480, 3 080, and 1 705 cm^{-1}, δ 0.2—0.4 (2 cyclopropyl H, m), 0.72 (3 H, s, 13-Me), 0.85 (6 H, d, 25-Me_2), 0.88 (3 H, d, 20-Me), and 0.98 (3 H, s, 10-Me) (Found: C, 80.7; H, 11.6. $C_{27}H_{46}O_2$ requires C, 80.5; H, 11.5%).

Dehydration of (1R,3S,10S)-10-*Hydroxy*-1,3-*cyclo*-5,10-*secocholestan*-5-*one* (9).—A solution of (9) (500 mg) in dimethylformamide (DMF) (6 ml)–pyridine (0.6 ml) was dehydrated with mesyl chloride (0.3 ml) at room temperature for 3 h and worked-up in the usual manner to give (1R,3S)-1,3-*cyclo*-5,10-*secocholest*-10(19)-*en*-5-*one* (10) (400 mg, 84%), m.p. 154—155° (from acetone–methanol); $[\alpha]_D^{20}$ +74° (*c* 1.45); $\nu_{max.}$ (KBr) 3 070, 1 700, and 1 634 cm^{-1}; δ 0.5—0.7 (2 H, m, cyclopropyl H), 0.74 (3 H, s, 13-Me), 0.86 (6 H, d, 25-Me_2), 0.92 (3 H, d, 20-Me), and 4.51 and 4.67 (each 1 H, CH_2=C) (Found: C, 84.4; H, 11.5. $C_{27}H_{44}O$ requires C, 84.3; H, 11.5%).

Dehydration of (1S,3R,10R)-10-*Hydroxy*-1,3-*cyclo*-5,10-*secocholestan*-5-*one* (11).—Alcohol (11) (10 mg) was treated with mesyl chloride in DMF–pyridine as described above to give (1S,3R)-1,3-*cyclo*-5,10-*secocholest*-10(19)-*en*-5-*one* (12) (8 mg, 84%) [i.r. spectrum was identical with spectrum of authentic (12)].

Opening of the Cyclopropane Ring.—(a) *In* (1R,3S)-1,3-*cyclo*-5,10-*secocholest*-10(19)-*en*-5-*one* (10). To a solution of (10) (100 mg) in aqueous acetone (9 : 1 v/v; 13 ml), toluene-*p*-sulphonic acid (58 mg) and potassium acetate (25 mg) were added and the mixture was heated under reflux for 18 h. After addition of water the mixture was extracted with ether and the organic layer was washed with aqueous sodium hydrogencarbonate and water, dried ($MgSO_4$), and evaporated *in vacuo* to dryness. The residue was chromatographed on a column of silica gel (5 g). Elution with light petroleum–benzene (1 : 1) afforded starting cyclopropane (10) (81 mg, 81%), m.p. 154° (from acetone–methanol). With benzene–ether (4 : 1) (*E*)-3α-hydroxy-5,10-secocholest-1(10)-en-5-one (4b) (18 mg, 17%) was obtained (i.r. and n.m.r. spectra were identical with spectra of an authentic sample).

(b) *In* (1S,3R)-1,3-*cyclo*-5,10-*secocholest*-10(19)-*en*-5-*one* (12). Cyclopropane (12) (200 mg), toluene-*p*-sulphonic acid (116 mg), and potassium acetate (50 mg) in aqueous acetone (9 : 1 v/v; 26 ml) were refluxed for 6 h and the product was worked up as described above. The residue was chromatographed on a column of silica gel (10 g). Elution with light petroleum–benzene (1 : 1) gave starting cyclopropane (12) (138 mg, 69%), m.p. 103° (from acetone–methanol). Benzene-ether (4 : 1) eluted (*E*)-3β-hydroxy-5,10-secocholest-1(10)-en-5-one (6b) (60 mg, 28%), m.p. 158° (undepressed by admixture with authentic sample).

Chromic Oxide Oxidation of the Stereoisomeric 3-*Hydroxy*-5,10-*secocholest*-1(10)-*en*-5-*ones* (3b)—(6b). *General Procedure.*—To a solution of alcohol (3b)—(6b) (100 mg) in diethyl ether (10 ml), chromic anhydride (500 mg) in water (10 ml) was added at room temperature, and the resulting mixture was stirred for 30 h. After isolation, the mixture was separated by chromatography on a column of silica gel (10 g). Elution with benzene–ether (99 : 1) gave (*Z*)- and (*E*)-5,10-secocholest-1(10)-ene-3,5-diones, respectively, and benzene–ether (4 : 1) eluted starting alcohols (3b)—(6b). The results are in Table 2.

(*Z*)-5,10-*Secocholest*-1(10)-*ene*-3,5-*dione* had m.p. 128° (from acetone); $[\alpha]_D^{20}$ +320° (*c* 1.00); $\nu_{max.}$ (KBr) 1 735, 1 720, and 1 705 cm^{-1}; δ 0.73 (3 H, s, 13-Me), 0.87 (6 H, d, 25-Me_2), 0.90 (3 H, d, 20-Me), 1.74 (3 H, d, 10-Me), 2.5—4.5 (4 H, m, 2α-, 2β-, 4α-, and 4β-H), and 5.20 (1 H, m, 1-H) (Found: C, 80.9; H, 11.2. $C_{27}H_{44}O_2$ requires C, 80.9; H, 11.1%).

(*E*)-5,10-Secocholest-1(10)-ene-3,5-dione [9] had m.p. 104° (from acetone); $[\alpha]_D^{20}$ −30° (*c* 1.00); $\nu_{max.}$ (KBr) 1 712 and 1 708 cm^{-1}; δ 0.69 (3 H, s, 13-Me), 0.84 (6 H, d, 25-Me_2), 0.88 (3 H, d, 20-Me), 1.67 (3 H, d, 10-Me), 2.6—3.6 (4 H, m, 2α-, 2β-, 4α-, and 4β-H), and 5.04 (1 H, m, 1-H) (Found: C, 81.2; H, 11.2%).

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