# Photo-induced Transformations. Part 69.[1] The Formation of Bridged Oxabicyclic Compounds by Intramolecular Radical Addition of Oxyl Radicals Generated from B-Homocholest-5-en-7a-ol Hypoiodites

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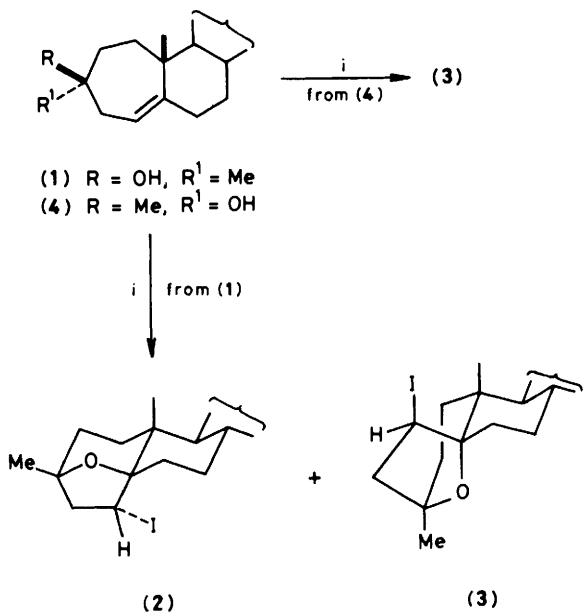
Reduction of B-homocholest-5-en-7a-one, synthesized by a Lewis acid-catalysed ring enlargement of cholest-5-en-7-one, with lithium aluminium hydride, gave B-homocholest-5-en-7aα-ol while reduction with sodium in ethanol afforded a more stable B-homocholest-5-en-7aβ-ol exclusively. The photo-induced reaction of the 7aα-ol in the presence of mercury(II) oxide and iodine gave 5,7aβ-epoxy-B-homo-5α-cholestane as the major product along with 5,7aα-epoxy-6β-iodo-B-homo-5α-cholestane and 5,7aβ-epoxy-6α-iodo-B-homo-5β-cholestane as the minor products. However, the photo-induced reaction of the 7aβ-ol in the presence of mercury(II) oxide and iodine gave 5,7aβ-epoxy-B-homo-5β-cholestane as the major product, with 5,7aβ-epoxy-6α-iodo-B-homo-5β-cholestane as the minor product. All these 5,7-epoxy-B-homocholestanes are formed by intramolecular addition of the oxyl radicals to the 5,6-double bond. The formation of 5,7aβ-epoxy-6α-iodo-B-homo-5β-cholestane from the 7aα-ol occurs *via* cyclization of a tetrahydropyranyl radical (D) which is formed by intramolecular combination of the allyl radical with carbonyl oxygen. This β-scission of the oxyl radical followed by a new type of radical cyclization was also found in the reaction of the oxyl radical generated from A-homocholest-4a-en-3β-ol.

In a previous paper,[2] we reported the photo-induced reactions of the hypoiodites of some steroidal seven-membered cyclic homoallyl alcohols, A-homocholest-4a-en-3-ols, in the presence of mercury(II) oxide and iodine. It was found that, unlike the corresponding reaction of cholest-5-en-3-ols,[3] intramolecular radical addition is a faster process than β-cleavage in the oxyl radical derived from the A-homocholest-4a-en-3-ols. Consequently, the photo-induced reaction of the hypoiodites of A-homocholest-4a-en-3α- and -3β-ol resulted in the formation of 3β,5-epoxy-4aα-iodo-A-homo-5β-cholestane and 3α,5-epoxy-4aα-iodo-A-homo-5β-cholestane, respectively. 3α-Methyl-A-homocholest-4a-en-3β-ol (1) and its 3α-isomer (4) likewise gave 3β,5-epoxy-3α-methyl-4aα-iodo-A-homo-5β-cholestane (2) and 3α,5-epoxy-3β-methyl-4aβ-iodo-A-homo-5α-cholestane (3) in good yields (Scheme 1).

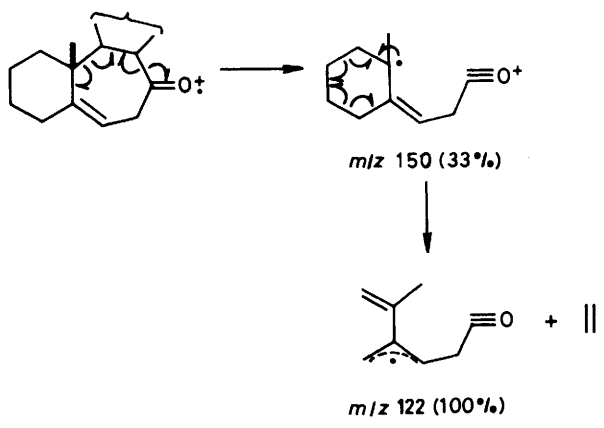



Scheme 1. *Reagents:* i, *hv*, $HgO–I_2$

Since the reaction appears to be of value for the synthesis of certain compounds having the 1-oxabicyclo[1.2.3]heptane skeleton, we have investigated the photo- and thermally-induced reactions of the hypoiodites of B-homocholest-5-en-7a-ols in the presence of mercury(II) oxide and iodine. The results are reported in this paper.

## Results and Discussion

*The Preparation of* B-*Homocholest-5-en-7a-ols and the Elucidation of Their Conformation by Molecular Mechanics Calculations.*—The B-homocholest-5-en-7a-one (6) employed for the preparation of B-homocholest-5-en-7a-ols was synthesized by the ring expansion of cholest-5-en-7-one (5)[4,5] with diazomethane in the presence of aluminium chloride in




Scheme 2.

35% yield. Boron trifluoride–diethyl ether, which was successfully used as a Lewis catalyst in the synthesis of A-homocholest-4a-en-3-one,[2,6] did not give rise to ring expansion and the starting material was recovered unchanged.

The mass spectrum of the ketone (6) showed two intense peaks at *m/z* 150 and 122 as well as the molecular ion peak at *m/z* 398. The probable formation and structure of these ions are shown in Scheme 2.

Reduction at room temperature of the 7a-one (6) with lithium aluminium hydride gave rise to a major amorphous alcohol (7) plus a small amount of the isomer (8) in the ratio 12 : 1; these were separated by preparative t.l.c. However, on reduction of the 7a-one (6) with sodium–ethanol under reflux, the more stable isomeric alcohol (8) was formed exclusively. The configurations of the hydroxy groups of the two alcohols (7) and (8) were established by means of $^1$H n.m.r. spectroscopy with the aid of a paramagnetic shift reagent. The effect on the 19-H shift in each alcohol in $CDCl_3$ on adding increasing amounts of Eu(dpm)$_3$ is shown in Figure 1. It can be seen that although the chemical shifts of 19-H in both alcohols move linearly to lower field on the addition of Eu(dpm)$_3$, the slope of the least-squares concentration line obtained from the alcohol (8) is much steeper than that obtained from (7). On the basis of this result, we assigned the configuration 7aα to the less stable 7a-alcohol (7), formed by reduction with lithium aluminium hydride, and 7aβ to the more stable isomer (8).

These assignments were in agreement with those obtained from empirical force-field calculations on the stability of the probable conformers of the two alcohols. The calculations (MM2) [7] of the relative energies of boat and chair forms of the B-ring of the 7a-one (6), the 7aα-alcohol (7), and 7aβ-alcohol (8) and the population of each are shown in the Table. Figure 2 shows ORTEP stereodrawings [8] of the boat and chair forms of the ketone (6) and the most stable C–OH rotamers in each B-ring conformer of the 7aα- (7) and the 7aβ-alcohol (8).

The boat conformation of the B-ring of the 7a-one (6) is more stable than the chair; the most stable of the 7a-ols is the 7aβ-ol, which has the boat conformation.

*Products of Irradiation of* B-*Homocholest-5-en-*7a-*ols in the Presence of Mercury*(II) *Oxide and Iodine* (*Scheme* 3).— Irradiation of the 7aα-ol (7) in benzene containing mercury(II) oxide and iodine (each 3 mol equiv.) with a 100-W high-pressure mercury arc for 5.5 h under nitrogen gave a mixture of products from which a major product, the crystalline cyclic ether (9) (71%), and two minor amorphous products (10) and (11) were isolated by preparative t.l.c. (Scheme 3).

The molecular formula of the major product (9) was established to be $C_{28}H_{48}O$ by an elemental analysis and mass spectrometric molecular weight determination. The i.r. spectrum showed the absence of hydroxy and carbonyl groups. The $^1$H n.m.r. spectrum showed a one-proton broad singlet at δ 3.94 which was ascribable to that arising from hydrogen attached to a carbon atom carrying oxygen. These spectral results were consistent with 5,7aα-epoxy-B-homo-5α-cholestane (9), formed by the intramolecular addition of a 7aα-oxyl radical to the double bond, followed by the abstraction of hydrogen from the solvent by the resultant carbon radical.

Of the two amorphous products, compound (10) (2%) which was more mobile on t.l.c. (2%) contained an iodine atom and the molecular formula was shown by means of mass spectrometry to be $C_{28}H_{47}IO$. Its $^1$H n.m.r. spectrum showed a one-proton broad doublet at δ 3.91 (*J* 7.1 Hz) and a one-proton doublet of doublets at δ 3.60 (*J* 8.9 and 10.4 Hz) ascribable to a hydrogen attached to a carbon carrying an oxygen and a hydrogen attached to a carbon carrying an iodine atom. The removal of the iodine atom of compound (10) with lithium aluminium hydride gave a compound identical with 5,7aα-epoxy-B-homo-5α-cholestane (9). These results confirmed the structure of compound (10) to be 5,7aα-epoxy-6ξ-iodo-B-homo-5α-cholestane. A comparison of the $^1$H n.m.r. spectra of compound (9) and iodine-free compound (10) showed that the signal arising from 19-H of (10) appeared at considerably lower field (δ 1.24) than that of (9) (δ 0.79). This shift to lower field is attributable to deshielding by the iodine atom, which must therefore have a 1,3-diaxial relationship with 19-H. The structure 5,7aα-epoxy-6β-iodo-B-homo-5α-cholestane is therefore the only one consistent with this $^1$H n.m.r. spectrum.

The other, less mobile minor product (11) (4%) was found to be identical with 5,7aβ-epoxy-6α-iodo-B-homo-5β-cholestane, a minor product obtained from the photo-induced reaction of B-homocholest-5-en-7aβ-ol in the presence of mercury(II) oxide and iodine (*vide infra*).

The 7aβ-ol (8) was then irradiated in the presence of mercury(II) oxide and iodine under the same conditions as for the 7aα-ol (7). This reaction gave a major product (12) (64%) accompanied by a minor product, shown to be (11)

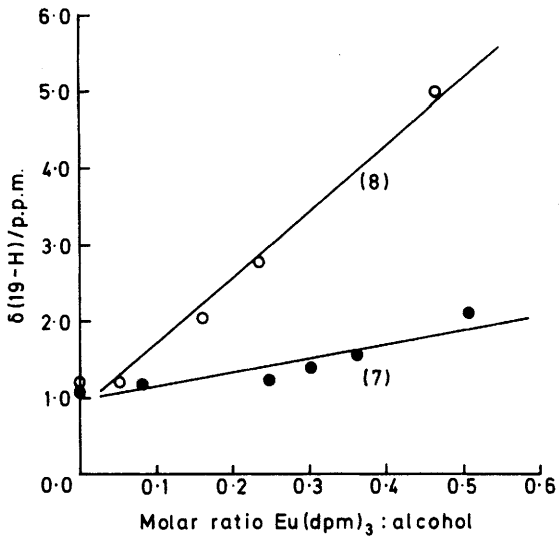



**Figure 1.** Variation in the chemical shift of 19-H of the 7aα- (7) and 7aβ-alcohol (8) in $CDCl_3$ with increasing concentration of Eu(dpm)$_3$. Straight lines shown are least-squares derived

**Table.** Enthalpies and strain energies (kcal mol$^{-1}$) and conformer populations of the ketone (6) and the alcohols (7) and (8) as calculated by the MM2 program [a,b]

| Conformation of B-ring | | Strain energy | $\Delta H_f$ | $\Delta\Delta H_f$ | Population (%) |
|---|---|---|---|---|---|
| Alcohol (7) and (8) | β-Boat | 46.397 | −117.58 | 0.00 | 87.90 |
| | α-Boat | 47.618 | −116.36 | 1.22 | 11.17 |
| | β-Chair | 52.322 | −116.65 | 7.15 | 0.00 |
| | α-Chair | 49.090 | −114.89 | 2.69 | 0.93 |
| Ketone (6) | Boat | 41.45 | −108.47 | 0.0 | 99.98 |
| | Chair | 46.45 | −103.47 | 5.0 | 0.02 |

[a] Calculations were carried out at the computing centre of Hokkaido University. [b] In the alcohols (7) and (8), three rotamers about the C–OH bond were calculated and the energy values given here are based on the populations of these rotamers.

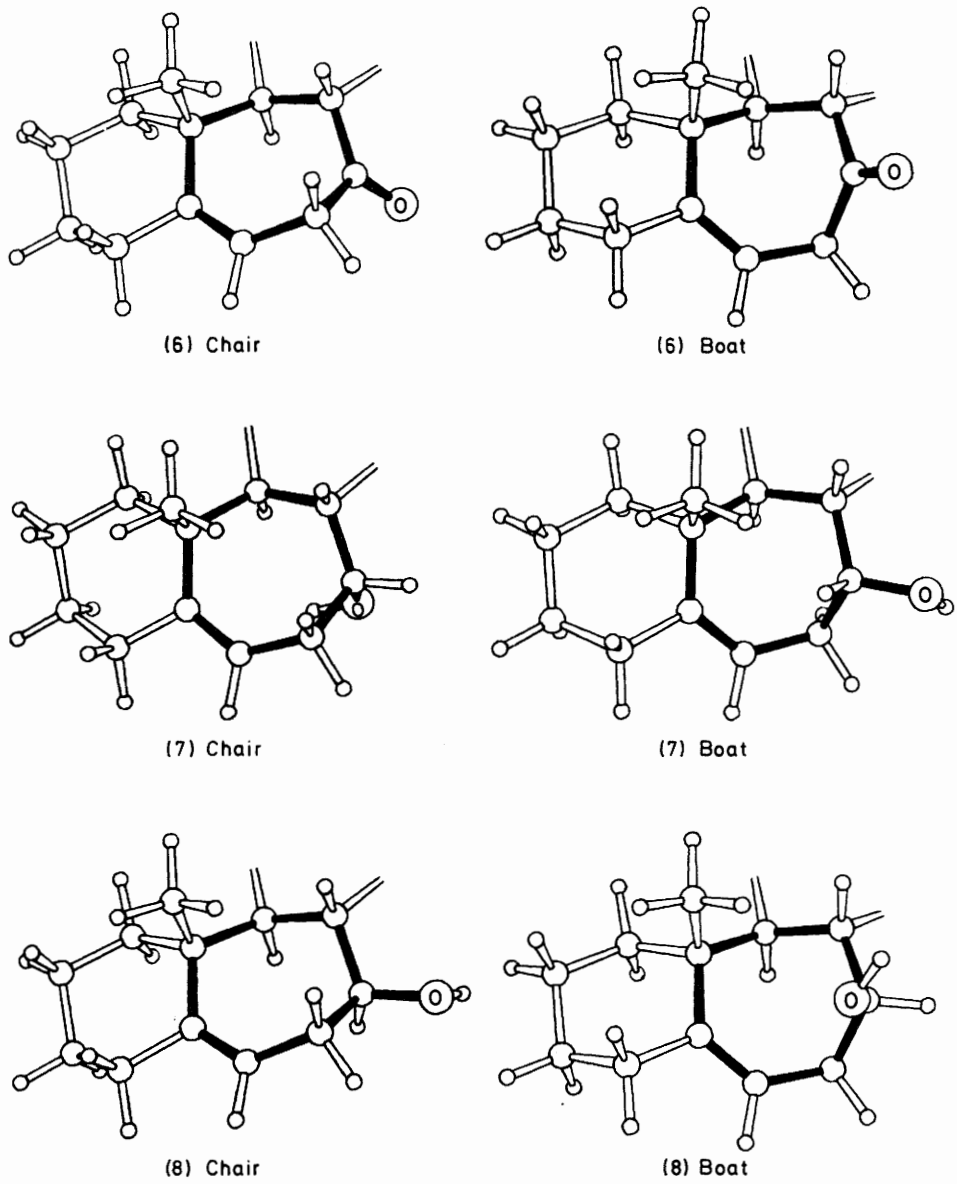


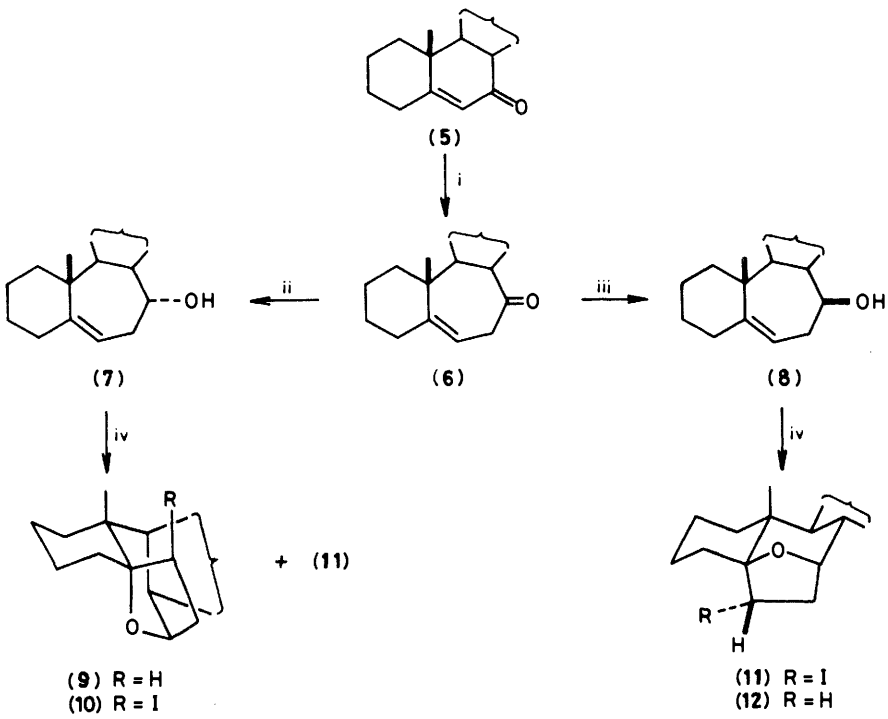

**Figure 2.** The ORTEP stereo-drawing of the boat and chair forms of the ketone (6), the 7aα-alcohol (7), and the 7aβ-alcohol (8). In the alcohols, the most stable C–OH rotamer of each B-ring conformers is shown

(16%). The molecular formula of the major product was shown to be $C_{28}H_{48}O$ by the mass spectrum and elemental analysis. Its $^1H$ n.m.r. spectrum showed a doublet of doublets at δ 4.06 (*J* 3.4 and 6.6 Hz) arising from a hydrogen attached to a carbon carrying an oxygen atom. The i.r. spectrum showed the absence of hydroxy and carbonyl groups. These spectral results were consistent with the structure 5,7aβ-epoxy-B-homo-5β-cholestane (12) formed by the intramolecular addition of a 7aβ-oxyl radical followed by hydrogen abstraction from the solvent by the resulting carbon radical. The $^1H$ n.m.r. spectrum of the iodine-bearing minor product showed a one-proton doublet of doublets at δ 3.77 (*J* 6.2 and 11 Hz) arising from a hydrogen attached to a carbon carrying an iodine atom, and a one-proton doublet of doublets at δ 3.97 (*J* 2.5 and 6.8 Hz) arising from a hydrogen attached to a carbon carrying an oxygen atom. Hydrogenolysis of the iodide with lithium aluminium hydride gave an iodine-free product which was identical with product (12). The iodine atom on C-6 is almost certainly α-oriented on the basis of *trans* addition to the double bond as well as the coupling constants of the signal at δ 3.77 (6-H) in the $^1H$ n.m.r. spectrum. The full structure of the minor product is thus shown to be 5,7aβ-epoxy-6α-iodo-B-homo-5β-cholestane (11).

*Products of the Thermal Decomposition of* B-*Homocholest-5-en-7aα-ol in the Presence of Mercury*(II) *Oxide and Iodine.*—The thermal reaction of the 7aα-ol (8) in benzene containing mercury(II) oxide and iodine at 60 °C for 5 h gave 5,7aα-epoxy-B-homo-5α-cholestane (9) and 5,7aα-epoxy-6β-iodo-B-homo-5α-cholestane (10), which were also obtained on photolysis; however the yields were lower, and 5,7aβ-epoxy-6α-iodo-B-homo-5β-cholestane (11), a minor product in the photo-induced reaction was not obtained.

## Discussion

The foregoing experiments confirm that the major reaction of the 7a-oxyl radicals generated from B-homocholest-5-en-7a-ol




**Scheme 3.** *Reagents:* i, $CH_2N_2$, $AlCl_3$; ii, $LiAlH_4$; iii, Na-$C_2H_5OH$; iv, *hν*, HgO-$I_2$

hypoiodites is intramolecular radical addition as in the case of the A-homocholest-4a-en-3-ol hypoiodites previously reported.[2] There are, however, two important differences in this case.

First, in contrast to the reaction of the ring A alcohol hypoiodites, the major products arising from the intramolecular radical additions described here are oxabicyclic compounds without an iodine atom. This difference is certainly due to steric effects; the approach of a bulky iodine source to the C-6 carbon radical centre on the steroid B-ring is appreciably more hindered than the approach to the C-4a carbon radical centre of the steroid A-ring. The formation of the oxabicyclic compounds (9) and (12) can only be explained by a radical pathway. However, the minor iodine-containing products (10) and (11) could be formed by an ionic or a radical pathway. The same is true of the ring A alcohol hypoiodites [2] from which only oxabicyclic compounds with an iodine atom can be obtained; it is very unlikely that such products are formed *via* an ionic pathway, since it would imply that an ionic mechanism operates in ring A while a radical mechanism occurs in ring B. We therefore conclude that all these oxabicyclic compounds, including those with iodine atoms described here and in ref. 2, are formed *via* radical pathways.

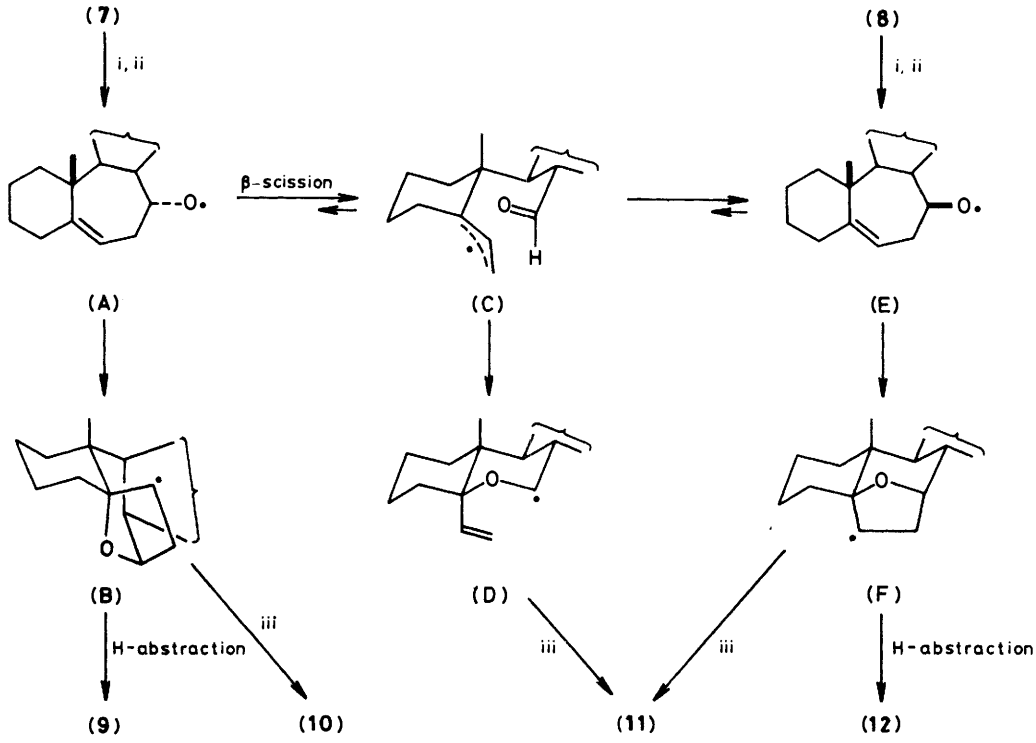
Secondly, the formation of 5,7aβ-epoxy-6α-iodo-B-homo-5β-cholestane (11) from B-homocholest-5-en-7aα-ol (7) (Scheme 3) is of mechanistic significance. Repeated experiments confirmed that while the 7aα-ol (7) gave an inverted iodide (11), the 7aβ-ol (8) gave neither of the inverted oxabicyclic compounds (9) and (10). We therefore re-examined the products of the reactions of A-homocholest-4a-en-3β-ol (1) and the 3α-ol (4).[2]

While the reaction of the 3α-ol (4) did not give even a trace of the inverted product 3β,5-epoxy-3α-methyl-4aα-iodo-A-homo-5β-cholestane (2), the 3β-ol (1) gave 8% of 3α,5-epoxy-3β-methyl-4aβ-iodo-A-homo-5α-cholestane (3), the inverted product, together with the normal addition product (2) (Scheme 1).

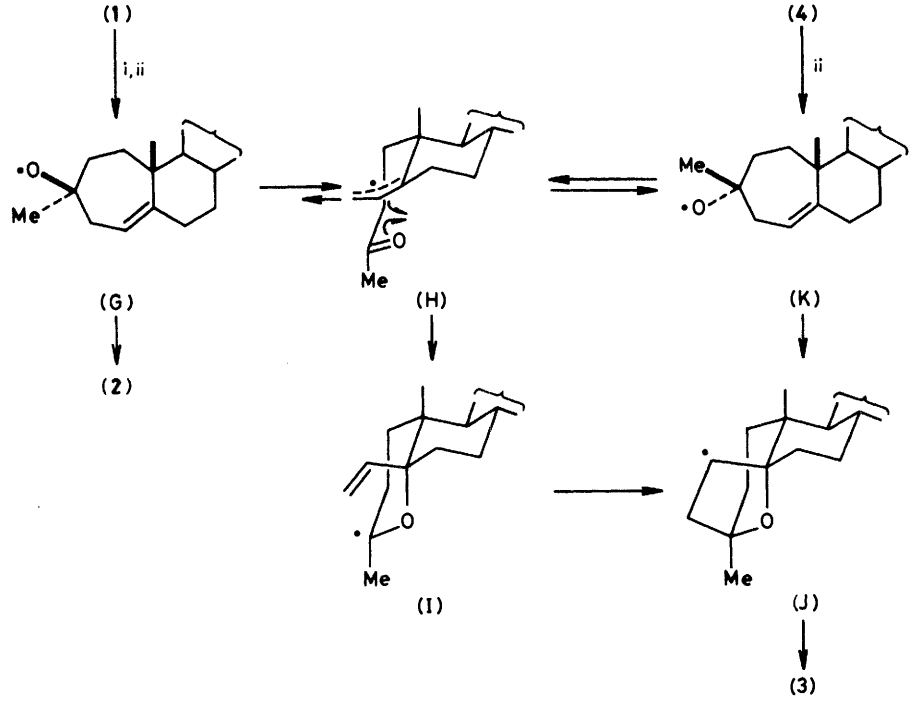
There are two possible pathways to these inverted products, as shown in Schemes 4 and 5. Thus, the inverted product (11) from the ring B alcohol hypoiodite (A) can be formed through either of the sequences (A) → (C) → (E) → (F) → (11) (path a) [9] or (A) → (C) → (D) → (11) (path b) and the inverted product (3) from the ring A alcohol hypoiodite (G) can be formed through either of the sequences (G) → (H) → (K) → (J) → (3) (path c) or (G) → (H) → (I) → (J) → (3) (path d).

The formation of product (11) from the α-ol (7) would be expected to follow path b, not path a, on the following basis. The photo-induced reaction of the 7aβ-ol hypoiodite *via* an intermediary carbon radical (F) gives a 16% yield of the product (11) together with a 64% yield of compound (12). If the 7aα-ol hypoiodite also reacts *via* the intermediate carbon-centred radical (F), the products (11) and (12) should be formed in the same ratio as obtained from the 7aβ-ol hypoiodite. As the reaction of the 7aα-ol (7) gave only product (11) it probably proceeds *via* path b. Thus, a carbonyl oxygen reacts with the C-5 terminus of the allyl radical (C) to form the intermediate (D); cyclization of the intermediate (D) and the addition of iodine then occur simultaneously to give the product (11). The tetrahydropyranyl radical has been reported previously.[10] Inspection of a Dreiding model of the allyl radical (C) shows that in the conformation leading to the A/B-*cis*-isomer of the tetrahydropyranyl radical (D) the 10β-methyl group and the C(9)–C(11) bond are almost eclipsed, and the conformation leading to the A/B-*trans*-isomer is therefore more stable. This conformational effect explains why neither of the inverted isomers (9) and (10) are formed from the 7aβ-ol hypoiodite.

In the reaction of the ring A alcohol, the product (3) from the 3β-ol hypoiodite would be expected to be formed *via* the intermediary allyl radical (H), as shown in Scheme 5. Inspection of a Dreiding model indicates that the radical (H) is most stable when the steric interactions between the C-10 substituent and the C-5 allyl radical moiety are minimized. This stable conformation is the one generated on β-scission of the isomeric oxyl radical (K). The recyclization of this



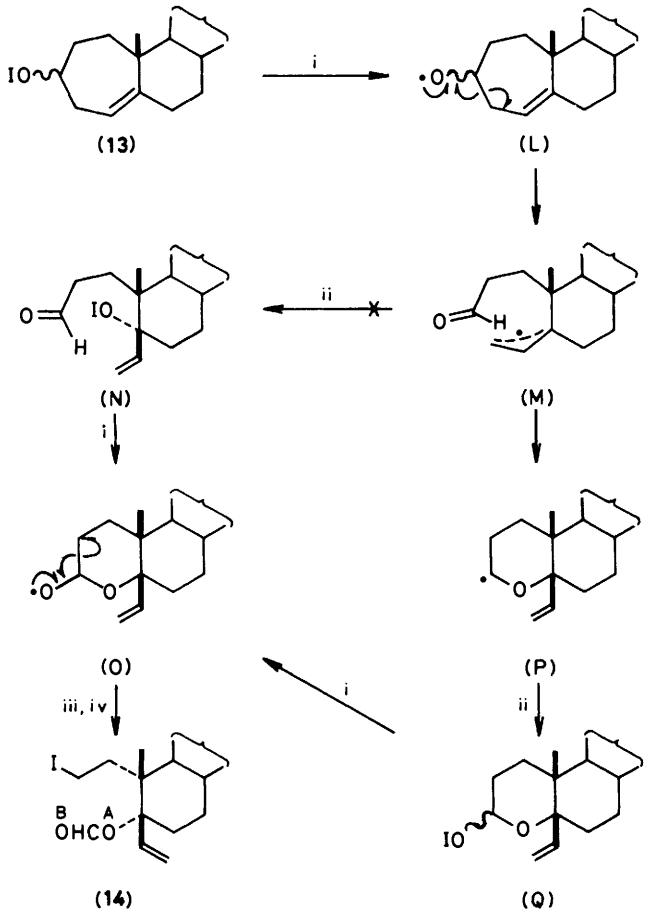

**Scheme 4.** *Reagents:* i, $I_2O$; ii, *hν* or heat; iii, ROI or $I_2$




**Scheme 5.** *Reagents:* i, $I_2O$; ii, *hν* or heat

stable conformation of (H) to give the oxyl radical (J) is not possible and the cyclization to give the oxyl radical (K) is also likely to be difficult. Thus, the inverted product (2) is not formed in the reaction of the 3α-ol hypoiodite (G), and the product (3) is probably formed *via* path d and not c.

*The Formation of a Formate from* A-*Homocholest*-4a-*en*-3ξ-*ol Hypoiodite* (13).—In a previous paper one of the present authors reported the formation of a formate (14) as a minor product in the photo-induced reaction of A-homocholest-4a-en-3ξ-ol hypoiodite (13). Based on the information available




**Scheme 6.** *Reagents:* i, *hν*; ii, $I_2O$; iii, β-scission; iv, $I_2$ or ROI

at the time of the report, a route *via* the intermediates (L)—(O), as shown in Scheme 6, was inferred. Our recent study using $^{18}O$-labelled mercury(II) oxide, however, indicated that oxygen A of the formate (14) originates from the starting hypoiodite (13). This excludes the intermediate (N), and the formate (14) is thus formed through intermediates (L), (M), (P), (Q), and (O), as shown in Scheme 6.

## Experimental

M.p.s were determined with a Yanagimoto micro m.p. apparatus. I.r. spectra were determined for Nujol mulls with a Hitachi 260-10 spectrophotometer unless stated otherwise. $^1H$ N.m.r. spectra were determined in $CDCl_3$ ($SiMe_4$ as internal reference) with a Hitachi R-22 spectrometer (90 MHz), a JEOL PS 100 high-resolution spectrometer (100 MHz), or a JEOL JNM FA-400 spectrometer (400 MHz). High and low resolution mass spectra were recorded with a JEOL JMS-D 300 spectrometer (70 eV) by the staff of the Faculty of Agriculture of this university. T.l.c. was carried out on Wako silica gel B-5.

*Synthesis of* B-*Homocholest-5-en-7a-one* (6).—To a solution of cholest-5-en-7-one [5] (3 g) in dichloromethane (*ca.* 3 ml) containing aluminium chloride (*ca.* 10 mg), was added dropwise a dichloromethane solution of diazomethane (*ca.* 7 ml) [prepared by shaking nitrosomethylurea (3 g) in dichloromethane (10 ml) and 40% aq. potassium hydroxide solution (10 ml), and drying the organic layer with potassium hydroxide], during 5 min and the solution was stirred for a further 5 min. After the precipitates had been filtered off, the volume of the solvent was reduced to 3 ml by a rotary evaporator. Treatment of this solution with a dichloromethane solution of diazomethane by the same procedure was repeated three more times. The dichloromethane solution was then washed with 5% aq. sodium carbonate, washed again with water, and dried ($Na_2SO_4$). After evaporation of the solvent the product was subjected to column chromatography (Merck Kieselgel 60, 90 g). Elution with benzene–hexane (2 : 1) gave a fraction which was recrystallized from methanol to give B-*homocholest-5-en-7a-one* (1.054 g, 35%), m.p. 95.5—97.0 °C (Found: C, 84.4; H, 11.6. $C_{28}H_{46}O$ requires C, 84.35; H, 11.63%); $\nu_{max.}$ 1 717 $cm^{-1}$ (C=O) 1 285, 1 253, and 1 040 $cm^{-1}$; δ (400 MHz) 0.73 (3 H, s, 18-$H_3$), 0.97 (3 H, s, 19-$H_3$), and 5.34 (1 H, d, *J* 10.3 Hz, 6-H); *m/z* 398 ($M^+$, 26.2%), 150 (52.0), and 122 (100).

B-*Homocholest-5-en-7aα-ol* (7).—A solution of the β,γ-unsaturated ketone (6) (532 mg) in diethyl ether (15 ml) containing lithium aluminium hydride (111 mg) was stirred for 3 h under nitrogen at room temperature. The reaction mixture was worked up by the usual method. The product was subjected to preparative t.l.c. with benzene to give the more t.l.c.-mobile *cholesten-7aα-ol* (7) (437 mg, 82%) and the less mobile 7aβ-ol (8) (37 mg). The 7aα-ol did not crystallize (Found: *m/z* 400.3637. $C_{28}H_{48}O$ requires *M*, 400.3703); $\nu_{max.}$ (neat) 3 460—3 560 (OH), 1 053, 1 031, and 738 $cm^{-1}$; δ (400 MHz) 0.68 (3 H, s, 18-$H_3$), 1.12 (3 H, s, 19-H), 3.77 (1 H, s, 7aβ-H), and 5.31 (1 H, dd, *J* 4.5 and 9 Hz, 6-H); *m/z* 400 ($M^+$, 15.4%) and 382 (100, $M^+ - H_2O$).

B-*Homocholest-5-en-7aβ-ol* (8).—To a refluxing solution of the β,γ-unsaturated ketone (6) (450 mg) in ethanol (15 ml) was added metallic sodium (1.88 g) in portions during 1.5 h. The solution was then heated under reflux for 2 h, the ethanol was removed under reduced pressure, and the residue was neutralized with 2M-hydrochloric acid and extracted with dichloromethane. The dichloromethane solution was washed with water and dried ($Na_2SO_4$). After the removal of the solvent, the product was subjected to preparative t.l.c. with benzene to give the *cholesten-7aβ-ol* (8) (292 mg, 65%) (Found: *m/z* 400.3702. $C_{28}H_{48}O$ requires *M*, 400.3702); $\nu_{max.}$ (neat) 3 370—3 550 (OH), 1 036, 739, and 680 $cm^{-1}$; δ (400 MHz) 0.71 (3 H, s, 18-$H_3$), 1.17 (3 H, s, 19-$H_3$), 3.87 (1 H, s, 7aα-H), and 5.15 (1 H, d, *J* 9 Hz, 6-H); *m/z* 400 ($M^+$, 8 8.6%), 385 ($M^+ - CH_3$, 55.1), 382 ($M^+ - H_2O$, 53.6), 95 (97.2) 81 (96.4), 55 (100), and 43 (85.6). A mixture (176 mg) of the starting ketone and the 7aβ-ol was also obtained by this t.l.c procedure.

*Irradiation of* B-*Homocholest-5-en-7aα-ol in the Presence of Mercury*(II) *Oxide and Iodine.*—The 7aα-ol (241 mg) in benzene (30 ml) containing mercury(II) oxide (406 mg) and iodine (236 mg) in a Pyrex tube and a second mixture comprising the 7aα-ol (253 mg) in benzene (32 ml) containing mercury(II) oxide (429 mg) and iodine (254 mg) in a Pyrex tube were flushed with nitrogen and irradiated for 5.5 h by a 100-W Hg arc lamp. The combined solution was filtered and the solution was washed with an aq. sodium thiosulphite solution, washed again with water, and dried ($Na_2SO_4$). Evaporation of the solvent left a product which was subjected to preparative t.l.c. with benzene to give four fractions (A—D) in the order of their mobility on t.l.c. The most mobile fraction A (15 mg, 2%) was amorphous 5,7aα-*epoxy*-6β-*iodo*-B-*homo*-5α-*cholestane* (10) (Found: *m/z* 526.2665. $C_{28}H_{47}OI$ requires *M*, 526.2670); $\nu_{max.}$ 1 262, 1 148, 1 028,

and 736 $cm^{-1}$; δ 0.62 (3 H, s, 18-$H_3$), 1.24 (3 H, s, 19-$H_3$), 3.60 (1 H, dd, *J* 8.9 and 10.4 Hz, 6α-H), and 3.91 (1 H, br d, *J* 7.1 Hz, 7aβ-H); *m/z* 526 ($M^+$, 0.3%), 511 ($M^+ - CH_3$, 0.3), 399 ($M^+ - I$, 100), 95 (91.6), 81 (49.9), 57 (47.5), 55 (48.7), and 43 (48.8).

Fraction B (24 mg, 4%) was 5,7aβ-epoxy-6α-iodo-B-homo-5β-cholestane (11); $\nu_{max.}$ 1 263, 1 234, 1 127, 1 032, 1 000, and 736 $cm^{-1}$; δ (90 MHz) 0.66 (3 H, s, 18-$H_3$), 1.06 (3 H, s, 19-$H_3$), 3.77 (1 H. dd *J* 6.2 and 11 Hz, 6β-H), and 3.97 (1 H, dd, *J* 2.5 and 6.8 Hz, 7aα-H); *m/z* 526 ($M^+$, 3.4%), 511 ($M^+ - CH_3$, 6.7), 399 ($M^+ - I$, 100), 95 (20.6), 81 (16.2), 57 (13.5) 55 (14.5), and 43 (13.9).

Fraction C (350 mg, 71%) was 5,7aα-*epoxy*-B-*homo*-5α-*cholestane* (9). After recrystallization from ethanol it had m.p. 46—47 °C (Found: C, 83.9; H, 12.1. $C_{28}H_{48}O$ requires C, 83.93; H, 12.08%); $\nu_{max.}$ 1 030 and 760 $cm^{-1}$; δ (100 MHz) 0.62 (3 H, s, 18-$H_3$), 0.79 (3 H, s, 19-$H_3$), and 3.95 (1 H, br s, $W_{\frac{1}{2}}$ 9 Hz, 7aβ-H); *m/z* 400 ($M^+$, 100%), 385 ($M^+ - CH_3$, 10.9), 287 (36.7), 95 (61.4), 81 (62.7), 55 (69.6), and 43 (58.6),

Fraction D (29 mg) was a mixture containing a small amount of 5,7aα-epoxy-B-homo-5α-cholestane (9).

*Irradiation of* B-*Homocholest*-5-*en*-7aβ-*ol* (8) *in the Presence of Mercury*(II) *Oxide and Iodine*.—The 7aβ-ol (255 mg) in benzene (33 ml) containing mercury(II) oxide (467 mg) and iodine (261 mg) in a Pyrex tube were flushed with nitrogen and irradiated for 12 h by a 100-W high-pressure Hg arc lamp. The reaction mixture was worked up as described for the reaction of the 7aα-ol. The product was subjected to preparative t.l.c. with benzene as solvent to give three fractions (A, B, and C). The most mobile fraction A (10 mg) was an unidentified substance. The fraction B (55 mg, 16%) was an 5,7aβ-epoxy-6α-iodo-B-homo-5β-cholestane (11). Fraction C (164 mg, 64%) was 5,7aβ-*epoxy*-B-*homo*-5β-*cholestane* (12) which was recrystallized from ethanol, m.p. 105—106 °C (Found: C, 83.6; H, 12.0. $C_{28}H_{48}O$ requires C, 83.93; H, 12.08%); $\nu_{max.}$ 1 055, 1 005, and 719 $cm^{-1}$; δ (100 MHz) 0.67 (3 H, s, 18-$H_3$), 1.02 (3 H, s, 19-$H_3$), and 4.06 (1 H, dd, *J* 3.4 and 6.6 Hz, 7aα-H); *m/z* 400 ($M^+$, 100%), 385 ($M^+ - CH_3$, 84.5), 371 (21.9), 95 (18.3), 81 (18.5), 55 (18.7), and 43 (16.0).

*Thermal Decomposition of* B-*Homocholest*-5-*en*-7aα-*ol Hypoiodite in the Presence of Mercury*(II) *Oxide and Iodine*.—The 7aα-ol (7) (195 mg) in benzene (25 ml) containing mercury(II) oxide (348 mg) and iodine (187 mg) in a vessel covered by aluminium foil was flushed with nitrogen and heated for 5 h while the temperature of the bath was kept at 60 °C. The reaction mixture was worked up as described for the photolysis. The product was subjected to preparative t.l.c. to give 5,7aα-epoxy-6β-iodo-B-homo-5α-cholestane (10) (36 mg, 14%) and 5,7aα-epoxy-B-homo-5α-cholestane (9) (58 mg, 30%) together with several minor products.

*Removal of Iodine from* 5,7aα-*Epoxy*-6β-*iodo*-B-5α-*cholestane* (10).—Iodide (10) (30 mg) in diethyl ether (7 ml) containing lithium aluminium hydride (20 mg) was stirred under nitrogen for 15 h. The usual work-up of the reaction mixture gave a product which was subjected to preparative t.l.c. to give 5,7aα-epoxy-B-homo-5α-cholestane (9) (5 mg), identical with the product (9) obtained from the photolysis, and several minor products.

*Removal of Iodine from* 5,7aβ-*Epoxy*-6α-*iodo*-B-*homo*-5β-*cholestane* (11).—The iodide (11) (39 mg) in diethyl ether (7 ml) containing lithium aluminium hydride (13 mg) was stirred for 17 h. The usual work-up gave a product which was subjected to preparative t.l.c. to give 5,7aβ-epoxy-B-homo-5β-cholestane (6 mg), identical with a specimen obtained from the photolysis, and several minor products.

*Irradiation of* 3α-*Methyl*-A-*homocholest*-4a-*en*-3β-*ol* (1) *in the Presence of Mercury*(II) *Oxide and Iodine*.—The 3β-ol (1) (302 mg) in benzene (32 ml) containing mercury(II) oxide (468 mg) and iodine (277 mg) in a Pyrex tube was flushed with nitrogen and irradiated for 2.5 h. The reaction mixture was worked up as described in ref. 2. The product was subjected to preparative t.l.c. with benzene–hexane (1 : 3) to give five fractions (A—E). The most mobile fraction A (32 mg, $R_F$ 10) and the third fraction B (28 mg, 8% based on the consumed starting material) were identical with authentic 3α,5-epoxy-3β-methyl-4aβ-iodo-A-homo-5α-cholestane (3) in every respect. Fraction D (185 mg, 52% based on consumed starting material) was 3β,5-epoxy-3α-methyl-4aα-iodo-A-homo-5β-cholestane (2). After recrystallization, it had m.p. 125—128 °C (lit.,[2] m.p. 128—130 °C). Fraction E (32 mg) was recovered starting material.

*Irradiation of* 3β-*Methyl*-A-*homocholest*-4a-*en*-3α-*ol* (4) *in the Presence of Mercury*(II) *Oxide and Iodine*.—The 3α-ol (4) (226 mg) in benzene (28 ml) containing mercury(II) oxide (421 mg) and iodine (302 mg) in a Pyrex vessel was irradiated by a 100-W high-pressure Hg arc lamp for 2 h. The reaction mixture was worked up as described in ref. 2. The product was subjected to preparative t.l.c. with benzene–hexane (1 : 3) to give two fractions A and B. Fraction A (16 mg) ($R_F$ 10) was an unidentified substance. The second fraction B (204 mg, 59%) was 3α,5-epoxy-3β-methyl-4aβ-iodo-A-homo-5α-cholestane (3), and after recrystallization it had m.p. 59—61 °C (lit.,[2] m.p. 56—58 °C). Fractions due to a more polar substance were carefully examined, but not even a trace of 3β,5-epoxy-3α-methyl-4aα-iodo-A-homo-5β-cholestane was detected.

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