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Photo- and Thermally-induced Radical Rearrangements of Hypoiodites of 3α- and 3β-Methyl-5-cholesten-3-ols in the Presence of Mercury(II) Oxide and Iodine or Silver(II) Oxide and Iodine

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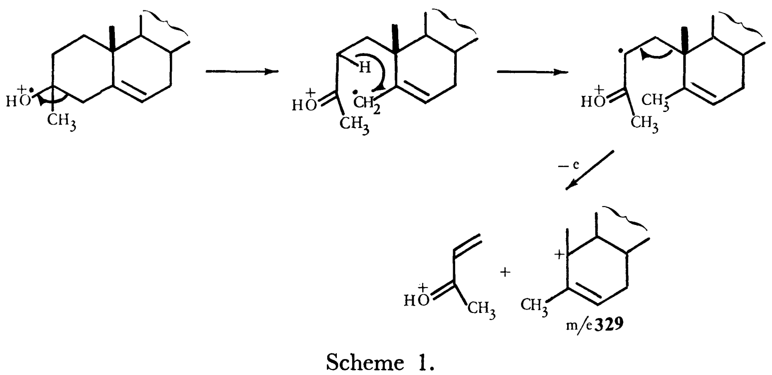
Hypoiodites of 3α- and 3β-methyl-5-cholesten-3-ols in benzene containing mercury(II) oxide and iodine gave 3α,5-epoxy-6β-iodo-3β-methyl-*A*-homo-4-oxa-5α-cholestane in 50—66% yield on irradiation or heating in the dark. Some minor products including the 6α-epimer were also found. The corresponding reaction with silver oxide and iodine reagent gave the same epoxide in 52% yield, together with a low yield of 3,4-seco-3-methyl-3-oxo-5-cholesten-4-al. Hydrogenolysis of the 6β-iodide with Pd–C as a catalyst gave 3α,5-epoxy-3β-methyl-*A*-homo-4-oxa-5α-cholestane (52% yield), together with the 6α-epimer arising from isomerization. The former, on treatment with boron trifluoride etherate and acetic anhydride in benzene, was transformed into 2-acetyl-3-methyl-5-acetoxymethyl-4-oxa-5β-cholestan-2-one. This was converted into 2β-acetyl-3α,5-epoxy-3β-methyl-4-oxa-*A*-homo-5α-cholestane by the treatment with aqueous methanolic potassium hydroxide.

In the previous paper, the photo- and thermally-induced radical rearrangements of cholesterol, epicholesterol, and 3,4,4-trimethylcholesterol hypoiodites in the presence of mercury(II) oxide and iodine were reported.[1] Cholesterol and epicholesterol hypoiodites in the presence of mercury(II) oxide and iodine were found to give 3α,5-epoxy-6β-iodo-*A*-homo-4-oxa-5α-cholestane and its 6α-isomer on irradiation and to give 3α,5-epoxy-6β-iodo-*A*-homo-4-oxa-5α-cholestane accompanied by *A*-homo-4-oxa-5-cholesten-3α-ol and 5-cholesten-3β-yl *A*-homo-4-oxa-5-cholesten-3α-yl ether on thermal reaction. The reactions of 3α,4,4-trimethyl-5-cholesten-3α-ol hypoiodite under comparable conditions gave 2α- and 2β-acetyl-4,4-dimethyl-3-oxa-5-cholestenes together with 3α,5-epoxy-*A*-homo-4-oxa-5α-steroids. Since the effects of alkyl substituents at their C-3 and C-4 positions appear to be appreciable, we investigated the photo- and thermally-induced radical rearrangements of hypoiodites of 3α- and 3β-methyl-5-cholesten-3-ols in the presence of mercury(II) oxide and iodine or silver(II) oxide and iodine. The results are reported in this paper.

Results

3α- And 3β-methyl-5-cholesten-3-ols (**1** and **2**) were prepared by previously described procedures.[2] The mass spectra of alcohols **1** and **2** were similar and exhibited a prominent peak at *m/e* 329 (69.3 and 100%). The suggested structure and genesis are shown in Scheme 1. Irradiation of 3β-alcohol **1** in benzene containing iodine and mercury(II) oxide (each 3 mol equiv.) with a 100-W high pressure mercury arc for 5 h under an argon atmosphere afforded a mixture of products (Scheme 2). In contrast to the case of cholesterol, a recrystallization of the product from methanol–diethyl ether readily gave an epoxide (**3**), mp 116.5—118.6 °C, in *ca.* 60% yield. The structure was ascertained to be 3α,5-epoxy-6β-iodo-3β-methyl-*A*-homo-4-oxa-5α-cholestane on the basis of the following spectral and chemical evidence. The mass spectrum of epoxide **3** showed a very weak molecular ion peak of *m/e* 541 and a prominent peak of *m/e* 415 (21.5%) assignable to M^+-I. Its infrared spectrum showed three 3H singlets at τ 8.60, 9.26, and 8.64 assignable to 3β-methyl, 18-H, and 19-H and an AB quartet centred at τ 6.58 and 5.77 (J=7.9 Hz) assignable to 4a-methylene protons. Besides these signals, the spectrum showed a 1-H triplet at τ 5.69 (J=3.2 Hz) assignable to a proton attached to a carbon bearing iodine (the 6α-H). Preparative TLC of the residue from the filtrate gave a further amount of epoxide **3** and a crystalline mixture. Although separation of the mixture into its components was unsuccessful, the NMR spectrum (see Experimental) indicated that it was a 1 : 1 mixture of 3α,5-epoxy-6α-



Scheme 1.

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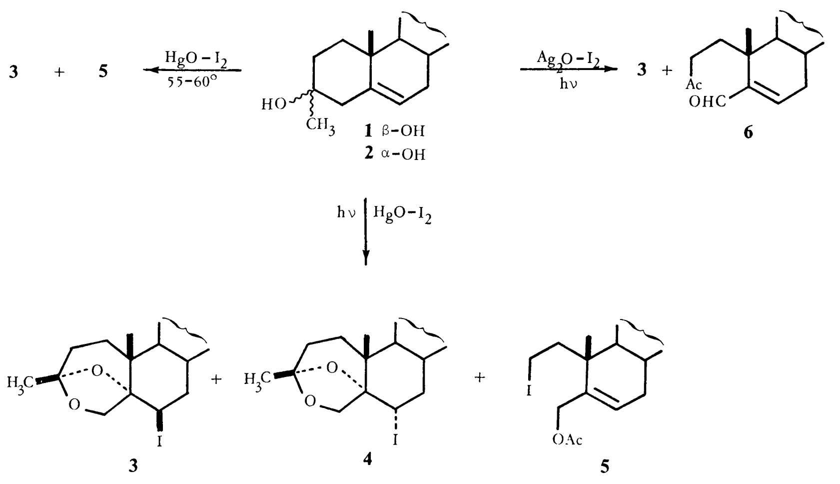


Scheme 2.

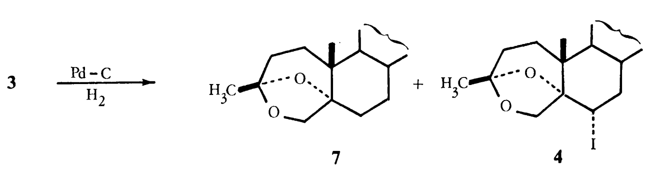
iodo-*A*-homo-4-oxa-5α-cholestane (**4**), obtained by a Pd-catalyzed isomerization of the 6β-isomer (*vide infra*), and 2-iodo-*A*-nor-2,3-seco-5-cholesten-3-ol acetate (**5**). The presence of the latter was indicated by a comparison of the signals with those of the ^{1}H NMR spectrum of 2-iodo-*A*-nor-2,3-seco-5-cholesten-3-ol formate.1) The yields of both compounds were about 2%.

Irradiation of 3α-alcohol **2** in benzene containing iodine and mercury(II) oxide under the conditions comparable to 3β-isomer **1** gave virtually the same products (Scheme 2). The isolated yield of pure crystalline epoxide **3** was 50% and a very minor amount of seco iodide **5** was also obtained.

The photo-reaction of 3β-alcohol **1** in benzene containing iodine and silver oxide in place of mercury(II) oxide was also attempted. This reaction was found to be very slow and more silver oxide and iodine were added to the solution after 5 and 48 h in the course of the reaction; 95 h was required to complete the reaction. A recrystallization and preparative TLC of the products gave crystalline epoxide **3** (52% yield) and a new amorphous compound (**6**) (4% yield) (Scheme 2). The NMR and IR spectra indicated the new compound should be formulated as 3,4-seco-3-methyl-3-oxo-5-cholesten-4-al (**6**); the IR spectrum exhibited three bands at 1720, 1691, and 1631 cm^{-1} in the carbonyl region which can be assigned to an acetyl and an α,β-unsaturated formyl groups. The NMR spectrum showed three 3H singlets at τ 8.00, 9.40, and 8.95 (assignable to 3-methyl, 18-H, and 19-H, a 1H double doublet (J=1.8 and 6.0 Hz) at τ 3.26 assigned to 6-H, and a 1H singlet at τ 0.81 assigned to the formyl proton.

The thermal decomposition of 3α-methyl-5-cholesten-3β-ol hypoiodite in the presence of mercury(II) oxide and iodine at 55—60 °C was also studied, and a higher yield of epoxide **3** (66%) was obtained. Not even a trace of 6α-iodo isomer **4** was detected in the products (Scheme 2). The absence of 6α-isomer in the products from the thermal reaction is also found for the reaction of cholesterol and 3,4,4-trimethylcholesterol.1)

*Some Reactions of 3α,5-Epoxy-6β-iodo-3β-methyl-*A*-homo-4-oxa-5α-cholestane (Schemes 3 and 4).* Iodo compound **3** was inert to base even under severe conditions.

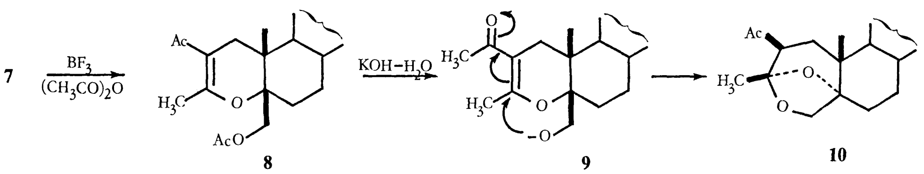


Scheme 3.

Thus, epoxide **3** in dioxan–water containing potassium hydroxide was refluxed for 25 h, but virtually no products resulting from elimination or substitution of iodine were formed and **3** was recovered unchanged.

Hydrogenolysis of iodo compound **3** with 10% Pd–C as a catalyst gave 3α,5-epoxy-3β-methyl-*A*-homo-4-oxa-5α-cholestane (**7**), mp 63.5—65.0 °C, in a 52% yield. Its NMR spectrum exhibited three 3H singlets at τ 8.57, 9.34, and 9.16 assigned to 3β-methyl, 18-H, and 19-H, and an AB quartet at τ 6.77 and 5.90 (J= 6.9 Hz). As would be expected, the signal due to the 19-H shifted upfield significantly in comparison with the corresponding signal of 6β-iodo compound **3**, proving that there is a β-oriented iodine atom in iodo compound **3**. Another amorphous product (**4**) was formed in this hydrogenolysis in a 26% yield. Iodine was still intact in product **4**; its NMR spectrum showed three 3H singlets at τ 8.52, 9.36, and 9.11 assigned to 3β-methyl, 18-H, and 19-H of 3α,5-epoxy-*A*-homo-4-oxasteroid, an AB quartet at τ 6.21 and 5.83 (J=8.3 Hz) assigned to the 4a-methylene protons, and a double doublet at τ 5.44 (J=5.3 and 12.0 Hz) assignable to a proton attached to a carbon bearing iodine. These results prove **4** to be a 6α-isomer of epoxide **3**. A homolysis of C–I bond is apparently followed by the recombination of iodine on the catalyst surface to give a more stable isomer **4**.

Treatment of iodine-free epoxide **7** with boron trifluoride etherate and acetic anhydride in benzene at room temperature for 30 min gave a crystalline product, mp 114—115 °C, in an 89% yield. All the spectral properties of the product were consistent with a dihydropyrane structure **8** (see Experimental). The mode of its formation from the epoxide has already been discussed in the previous paper.1) Hydrolysis of product **8** with aq methanolic potassium hydroxide



Scheme 4.

Table. NMR parameters (100 MHz) for the 3-methyl-5-cholestenes and the reaction products in $CDCl_3$ solution (chemical shifts τ and splittings Hz)

Compd	3-Methyl	4 or 4a-Methylene	6-H	18-H	19-H	Others
1	8.88(s)	a)	4.74(br s)	9.32(s)	8.98(s)	
2	8.99(s)	a)	4.61(br s)	9.29(s)	8.75(s)	
3	8.60(s)	6.58(d) and 5.77(d) (7.9)	5.69(br t, 3.2)$^{b)}$	9.26(s)	8.64(s)	
4	8.52(s)	6.21 5.83 (2d, 8.3)	5.44(dd, 5.3 and 1.2)	9.36(s)	9.11(s)	
6	8.00(s)	—	3.26(dd, 1.8 and 6.0)	9.40(s)	8.95(s)	0.81(s) (CHO)
7	8.57(s)	6.77 5.90 (2d, 6.9)	a)	9.34(s)	9.16(s)	
8	7.92(s)	5.98 5.78 (2d, 12.3)	a)	9.34(s)	8.91(s)	OAc 7.78(s) Ac 7.78(s)
10	8.60(s)	6.69 5.83 (2d, 7.7)	a)	9.33(s)	9.09(s)	Ac 7.83(s) 2α-H 7.23(dd, 5.44 and 12.0)

a) Unassignable. b) Superimposed with one of the 4a-methylene protons.

at room temperature for 1.5 h gave a compound (**10**), mp 131—134 °C, devoid of hydroxyl band in its IR spectrum. The mass, IR, and NMR spectra of product **10** were in full agreement with this structure: 2β-acetyl-3α,5-epoxy-3β-methyl-4-oxa-*A*-homo-5α-cholestane (**10**) formed by an intramolecular Michael addition of the first formed alcohol (**9**). Its IR spectrum showed a band at 1711 cm^{-1} due to an acetyl group and the NMR spectrum showed three 3H singlets assigned to 3β-methyl, 18-H, and 19-H, and an AB quartet assignable to 4a-methylene protons. Besides these signals, the spectrum showed a 3H singlet at τ 7.83 and a 1H double doublet at τ 7.23 (J= 5.4 and 12.0 Hz) assignable to the 2α-H. Epoxide **7** is formed in a manner entirely analogous to its 3-demethyl homologue.[1]

Discussion

The paths by which 3α,5-epoxide [*e.g.* **3** and **4**] are formed have been discussed in the previous paper.[1] Our experiments again confirmed the generality of the reaction, but the effects of a substitution by a methyl group at the C-3 of 3-hydroxy-Δ^5-steroids on the type of products and their relative yields are clear.

Thus, although thermal and photoinduced reactions of 3α- and 3β-methylcholesterol hypoiodites in the presence of mercury(II) oxide and iodine afford the products parallel to those in the corresponding reaction of cholesterol, the formation of 6β-iodo compound (*e.g.* **3**) as a single major product is noteworthy. Another feature of the present reaction is the absence of 3-oxa-5-cholesten-3β-ol under the experimental procedures comparable to the present reactions. As we suggested 4,4-dimethyl groups may be necessary in order to achieve an appropriate geometry of an intermediate to lead to 3-oxa-5-cholestenes. The absence of the 6α-isomer **4** in the products from the thermal reaction of 3α- and 3β-methylcholesterol hypoiodites[1] was again confirmed. The formation of 3α,5-epoxy-6α-iodo-*A*-homo-4-oxa-5α-steroids and 3α,5-epoxy-*A*-homo-4-oxa-5α-steroid-6-ene has been concluded to arise from an ionic reaction of intermediate carbonium ions.

No dimeric acetal, obtained from cholesterol, was formed in the thermal reaction of 3α- and 3β-methylcholesterol hypoiodites. The 3-methyl group in these hypoiodites hinders the formation of dimeric acetal in the thermal reaction and apparently facilitates the intramolecular reaction to 3α,5α-epoxy-*A*-homo-4-oxa-steroids.

Experimental

For instruments used and general procedures see Ref. 1. Mass spectra of compounds **1**, **2**, **7**, **8**, and **10** were recorded in the Faculty of Agriculture with a Hitachi JMS-D 300 spectrometer (ionizing voltage 70 eV). Mass spectra of compounds **3** and **4** were recorded in the Faculty of Pharmaceutical Sciences with a Hitachi RMU-6E spectrometer (ionizing voltage 70 eV).

3α- And 3β-Methyl-5-cholesten-3-ols ***1*** *and* ***2***. These compounds were prepared by a described procedure.[4] 3β-Alcohol **1** mp 168.5—170.0 °C, (lit,[4] mp 167—168 °C); $[\alpha]^{34}_{D}$ −28.8° (*c* 1.3 in $CHCl_3$) (lit,[4] $[\alpha]^{25}_{D}$ −30° (*c* 1.25 $CHCl_3$); MS, *m/e* (rel intensity) 400 (M^+, 4.1%), 382 (M^+-H_2O, 100), 36.7 ($M^+-H_2O-CH_3$, 10.0), 329 (69.3), 147 (20.2), 121 (24.6), 119 (25.6), 107 (21.3) 95 (45.3), 81 (26.7), 57 (19.9), 55 (20.1), and 43 (19.9); for NMR see Table, 3α-Alcohol **2**. Mp 118.0—120.0 °C (lit,[4] mp 119—120 °C); $[\alpha]^{29}_{D}$ −27.2° (*c* 0.9 $CHCl_3$) (lit,[4] $[\alpha]^{25}_{D}$ −29° (*c* 0.94 $CHCl_3$); MS, *m/e* (rel intensity) 400 (M^+, 5.6%), 382 (M^+-H_2O, 85.9), 367 (6.8), 329 (100), 147 (19.0), 121 (25.4), 119 (34.3), 107 (22.3), 95 (39.9), 81 (25.7), 57 (20.5), 55 (23.8), and 43 (34.3); for NMR see Table.

Rearrangement of 3α-Methyl-5-cholesten-3β-ol Hypoiodite in the Presence of Mercury(II) Oxide and Iodine. By Irradiation. 3β-Alcohol **1** (1 g, 2.5 mmol), mercury(II) oxide (1.62 g, 7.5 mmol), and iodine (1.75 g, 7.5 mmol) in benzene (150 ml) were irradiated under an argon atmosphere with a 100-W high pressure mercury arc for 5 h. The solution was once filtered and the evaporation of the solvent from the filtrate at below 30 °C left a residue which was extracted with chloroform (200 ml). The chloroform solution was washed with 5% aq sodium hydrogensulfite, water saturated with sodium chloride, and water successively, and dried (Na_2SO_4). Removal of the solvent left a residue which was recrystallized from a mixture of diethyl ether and methanol to give epoxide **3**, mp 112—114 °C, (749 mg). The specimen for analysis was obtained by recrystallizing it from methanol. Mp 116.5—118.5 °C. (Found: C, 61.82; H, 8.79; I, 23.58%. Calcd for $C_{28}H_{47}O_2I$: C, 61.98; H, 8.73; I, 23.39%); $[\alpha]^{34}_{D}$ −36.0° (c 1.0 $CHCl_3$); IR, 1198, 1175, 1121, 1024, and 865 cm^{-1}; MS, *m/e* (rel intensity) 541 (M^+, 0.5%), 415 (M^+-I, 21.5), 373 (100), 355 (16.7), 327 (42.9), 57 (26.2), and 43 (52.4); for NMR see Table. The filtrate from the first recrystallization was evaporated to yield a residue (570 mg). It was subjected to preparative TLC with a 2:3 mixture of hexane–benzene. The most mobile fraction (154 mg) showed two spots on TLC. This fraction was again subjected to preparative TLC to afford two fractions. The more mobile fraction was a crude acetal **3** (70 mg), which was recrystallized from methanol to yield a further amount of acetal **3** (59 mg). The less mobile fraction (47 mg) was a mixture; its NMR spectrum indicated it was almost certainly a 1:1 mixture of 3α,5-epoxy-6α-iodo-3β-methyl-*A*-homo-4-oxa-5α-cholestane and 3-acetoxy-2-iodo-*A*-nor-2,3-seco-5-cholesten-3-ol acetate. It showed three singlets at τ 9.35 (18-H), 9.09 (19-H), and 8.51 (3-methyl), an AB quartet (C-4a methylene) at τ 5.82 and 6.20 (*J*=8 Hz), and a double doublet at τ 5.48 (*J*=5 and 12 Hz) (6β-H) [a doublet at higher field was superimposed with a signal due to C-3 methylene of product **5**] of product **4**. In addition to these signals, it showed three singlets at τ 9.32, 9.01, and 7.86, a broad singlet at τ 5.48, and a diffused doublet at τ 4.11, which could be assigned to 18-H, 19-H, 3-acetoxyl, 3-H, and 6-H of seco iodide **5**. An attempted separation of these two products by means of preparative TLC was unsuccessful. More polar fractions (396 mg) were an intractable mixture.

Thermal Reaction: A reaction mixture in the same scale as that for the photo-reaction was heated at 55—60 °C under an argon atmosphere for 3 h and worked up as usual. The crude mixture (1.38 g) was recrystallized from diethyl ether–methanol to yield an acetal **3**, mp 113—115.5 °C (862 mg). Removal of the solvent left a residue (441 mg) which was subjected to preparative TLC. A fraction (52 mg) of acetal **3** was recrystallized to yield the acetal (37 mg). The less mobile fraction (22 mg) was identified to be seco ketone **6** on the basis of the NMR spectrum. In contrast to the photo-reaction results, 6α-iodo isomer **5** was absent in the product, as indicated by TLC.

Photoinduced Rearrangement of 3β-Methyl-5-cholesten-3α-ol Hypoiodite in the Presence of Mercury(II) Oxide and Iodine. 3α-Alcohol **2** (400 mg, 1 mmol), mercury(II) oxide (651 mg, 3 mmol), and iodine (762 mg, 3 mmol) in benzene (60 ml) were irradiated under an argon atmosphere for 3 h. After the usual work-up, a crude product (620 mg) was recrystallized from diethyl ether–methanol to give acetal **3** (234 mg), mp 112—115 °C. The residue from the filtrate was subjected to preparative TLC with a 2:3 mixture of hexane–benzene. The most mobile fraction (50 mg) was recrystallized to yield acetal **3** (35 mg). The next mobile fraction (10 mg) was a seco iodide, as judged by its NMR spectrum. From the less mobile fraction, the starting material (7 mg, 2%) was recovered unchanged.

*Photoinduced Rearrangement of 3β-Alcohol **1** in the Presence of Silver(II) Oxide and Iodine.* 3β-Alcohol **1** (300 mg, 0.75 mmol), silver oxide (552 mg, 2.25 mmol), and iodine (796 mg, 2.25 mmol) in benzene (40 ml) were irradiated under an atmosphere of argon for 95 h. In the course of the reaction, further amounts of silver(II) oxide and iodine were added [silver(II) oxide 340 mg and iodine 460 mg at the period of 5 h and silver(II) oxide 180 mg and iodine 400 mg at the period of 48 h]. Work-up of the reaction mixture gave a crude product (392 mg), which was recrystallized from a mixture of acetone and methanol to yield acetal **3** (203 mg), mp 116.5—118.5 °C. A residue from the filtrate was subjected to preparative TLC with a 2:3 mixture of hexane and benzene. The most mobile fraction (17 mg) was recrystallized to give acetal **3** (10 mg). The least mobile fraction (50 mg) was again subjected to preparative TLC to afford an amorphous α,β-unsaturated aldehyde **6**. IR, (neat) 1720 (acetyl), 1691 and 1631 (α,β-unsaturated formyl), 1463, 1376, 1361, 1258, 1161, and 805 cm^{-1}; for NMR spectrum see Table.

*Hydrogenolysis of Epoxide **3** with 10% Palladium on Carbon Catalyst.* Epoxide **3** (543 mg) in a mixed solvent of ethanol (18 ml) and benzene (20 ml) containing potassium acetate (80 mg) and a 10% Pd–C catalyst (200 mg) was hydrogenated under an atmospheric pressure for 28 h. At the period of 24 h, a further amount of the catalyst (50 mg) was added. After removal of the catalyst and the solvent, the residue was dissolved in diethyl ether. The solution was washed with water and dried (Na_2SO_4). The residue (470 mg) was subjected to preparative TLC to give three fractions. The most mobile fraction (140 mg) was an amorphous 6α-epimer **4**. $[\alpha]^{20}_{D}$ −6.8° (*c* 2.0 $CHCl_3$); IR, no hydroxyl and carbonyl bands; 1276, 1234, 1134, 1039, and 734 cm^{-1}; MS *m/e* (rel intensity) 542 (M^+ +1, 0.3%), 541 (M^+, 0.1), 415 (M^+-I, 96), and 99 (100); for NMR spectrum see Table. The next mobile fraction (260 mg) was recrystallized from a mixture of diethyl ether and methanol to give 3α,5α-epoxide **7** (215 mg) in 2 crops, mp 61.5—63.0 °C. The specimen for analysis, mp 63.5—65.0 °C was obtained by further recrystallizations. (Found: C, 80.40; H, 11.70%. Calcd for $C_{28}H_{48}O_2$: C, 80.71; H, 11.61%), $[\alpha]^{20}_{D}$ +10.9 (*c* 1.0 $CHCl_3$); IR, 1120, 1028, and 866 cm^{-1}; MS *m/e* (rel intensity) 416 (M^+, 7.5%), 387 (55.9), 356 (28.6), 345 (100), 327 (96.7), 215 (25.1), 120 (26.2), 95 (29.2), 81 (28.1), 55 (25.3), and 43 (31.3); for NMR spectrum see Table.

*The Reaction of 3α,5α-Epoxide **7** with Boron Trifluoride Etherate and Acetic Anhydride.* 3α,5α-Epoxide (105 mg, 0.25 mmol), acetic anhydride (0.2 ml, 2 mmol), and boron trifluoride etherate, (0.05 ml, *ca.* 0.39 mmol) in benzene (10 ml) were stirred for 30 min at 22 °C. The solution was neutralized by the addition of aq sodium hydrogencarbonate and was extracted with diethyl ether. The solution was washed with aq sodium hydrogencarbonate solution and water, and dried (Na_2SO_4). Removal of the solvent gave a dihydropyrane derivative **8** (109 mg) in two crops. The specimen for analysis was obtained by further recrystallizations and melted at 114—115 °C. (Found: C, 76.53; H, 10.36%. Calcd for $C_{32}H_{52}O_4$: C, 76.75; H, 10.43%); $[\alpha]^{22}_{D}$ −7.7° (*c* 0.9 $CHCl_3$); UV λ_{max} (ethanol) 268 nm (ε; 11500); IR, 1754 (acetyl), 1675 and 1583 (RO–C=C–Ac), 1240, and 1043 cm^{-1}; MS *m/e* (rel intensity) 500 (M^+, 6.5%), 397 (5.2), 328 (4.9), 327 (9.6), 95 (14.2), and 43 (100); for NMR spectrum see Table.

Hydrolysis of Dihydropyrane Derivative 8. Dihydropyrane derivative **8** (20 mg) in a mixture of diethyl ether (1 ml) and methanol (1 ml) containing water (1.1 ml) and potassium hydroxide (50 mg) was stirred for 1.5 h at room temperature. The solution was extracted with diethyl ether (20 ml). The organic layer was washed with dilute hydrochloric acid and water and dried (Na_2SO_4). The crude product (14 mg) was recrystallized from methanol to yield 3α,5α-epoxy-*A*-homo-4-oxa-steroid **10**, mp 131—134 °C. Recrystallization raised the melting point to mp 134—137 °C; IR, 1711 (acetyl), 1175 and 1026 cm^{-1}; MS *m/e* (rel intensity) 458 (10.7%), 440 (20.9), 398 (38.8), 345 (25.0), 328 (100), 327 (37.8), 247 (19.1), 215 (45.7), 121 (23.3), 120 (43.9), 119 (23.9), 95 (36.4), 81 (24.3), and 43 (55.4); for NMR spectrum see Table.

The authors are grateful to Mrs. Tomoko Okayama for the measurements of the ^{1}H NMR spectra.

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