Intramolecular Hydrogen Abstraction. Hypervalent Organoiodine Compounds, Convenient Reagents for Alkoxyl Radical Generation

Pedro de Armas, José I. Concepción, Cosme G. Francisco, Rosendo Hernández, José A. Salazar, and Ernesto Suárez
Instituto de Productos Naturales Orgánicos del C.S.I.C., Carretera de La Esperanza 2, La Laguna, Tenerife, Canary Islands, Spain

The photolyses of 5α-cholestane-3β,6β-diol 3-acetate (1), 5α-cholestan-2β-ol (4), 5α-cholestan-4β-ol (8), (20R)-pregn-5-ene-3β,20-diol 3-acetate (19), (20S)-pregn-5-ene-3β,20-diol 3-acetate (21), and dihydrotigogenin 3-acetate (25) in the presence of iodine and various hypervalent organoiodine compounds lead to alkoxyl radicals which undergo intramolecular hydrogen abstraction to produce, in most cases, 1,4-iodohydrins and tetrahydrofuran derivatives.

The chemistry of hypervalent organoiodine compounds has been, over the past decade, an active area of research.[1] A variety of organic tri- and penta-valent iodine compounds have become effective reagents, not only to promote broad types of oxidative conversions but also in other reactions such as halogenations, arylations, *etc.* On the other hand, the intramolecular remote functionalization on non-activated atoms initiated by alkoxyl radicals has been the subject of numerous studies.[2] Alkoxyl radicals have been generated by photolysis of nitrites (Barton reaction) or by reaction of alcohols with a variety of oxidizing agents such as *N*-iodosuccinimide, mercury(II) oxide, and acetyl derivatives of Pb^{IV}, Hg^{II}, and Ag^{I}, usually in the presence of iodine (hypoiodite reaction). The lead tetra-acetate (LTA)–iodine procedure has been the most frequently used and appears to give the best yields.

In a preliminary communication we have shown[3] that (diacetoxyiodo)benzene (DIB) in the presence of iodine reacts with alcohols to produce alkoxyl radicals, presumably *via* a hypoiodite intermediate, which are able to abstract hydrogen atoms intramolecularly from suitably positioned non-activated carbons. The reaction was illustrated by appropriate substrates in the steroid field. We now report full details of these experiments and the extension of other examples, as well as the results of the study of the photolysis of 5α-cholestane-3β,6β-diol 3-acetate (1) with several organoiodine compounds in the presence of iodine.

These reagents, especially DIB, proved to be more efficient and convenient than the heavy-metal derivatives usually employed in such reactions.

We presumed that the alkoxyl radicals are formed by reaction of the alcohols with the acetyl hypoiodite produced *in situ* by reaction of the organoiodine compound with iodine.

$$PhI(OAc)_2 + I_2 \longrightarrow PhI + 2AcOI$$
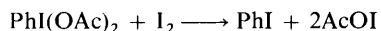
In fact, the reaction of DIB and iodine with carboxylic acids produces acyl hypoiodites which iododecarboxylate, constituting a method for the preparation of alkyl halides from acids.[4] It has also been reported that the thermal decomposition of (diacetoxyiodo)arenes, in the absence of iodine, gives a number of compounds that can be explained considering the formation of acetyl hypoiodite and acetoxyl radicals as intermediates.[5]

Acetyl hypoiodite has never been isolated but has been postulated as an intermediate in numerous reactions, such as the Hunsdiecker,[6] modified Hunsdiecker,[7] and in the decomposition, in the presence of iodine, of metal acetates such as silver acetate, mercury(II) acetate, and LTA.[2]

Results and Discussion

The reaction of 5α-cholestane-3β,6β-diol 3-acetate (1) with mono-, tri-, and penta-valent organoiodine compounds in the presence of iodine was performed by photolysis with visible light (2 × 100-W tungsten-filament lamps) in cyclohexane under the

(1) R = α-H, β-OH
(2) R = O

(3)

(4) R = H
(5) R = I

(6)
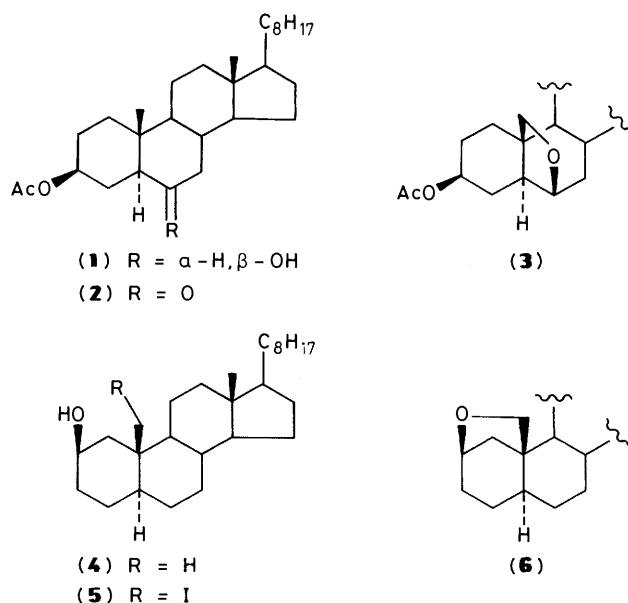
conditions summarized in Table 1. The choice of the steroidal alcohol (1) as a model for this reaction was based on the rigid 1,3-diaxial orientation between the hydroxy group and the carbon to be functionalized (10-Me) and, furthermore, on comparative bases, as the reactions of this alcohol with several reagents and conditions can be found in the literature.[8]

The reaction of alcohol (1) with the monovalent iodine compound tetrabutylammonium diacetoxyiodate(I) led to a mixture of the functionalized compound (3) and the ketone (2) (Table 1, entry 1). No hydrogen abstraction was detected when this reagent was used in absence of iodine but 40% of the ketone (2) was formed instead (Table 1, entry 2).

The reaction proceeded well with three of the four different trivalent organoiodine reagents utilized: DIB, (bistrifluoroacetoxyiodo)benzene (TFIB), and iodosylbenzene and did not work with *o*-iodosylbenzoic acid (Table 1, entries 3—8). The

Table 1. Reaction of 5α-cholestane-3β,6β-diol 3-acetate (1) with hypervalent iodine reagents[a]

Entry	Reagent (mmol)	Iodine (mmol)	Conditions (min; °C)	roducts (yield %)
1	Bu$^n_4$N$^+$ $^-$I(OAc)$_2$ (2.2)	2.0	180; reflux	(3) (85), (2) (10)
2	Bu$^n_4$N$^+$ $^-$I(OAc)$_2$ (1.1)	0	30; 45	(1) (60), (2) (40)
3	DIB (1.1)	1.0	50; 40	(3) (90)
4	DIB (1.1)	0.3	180; 40	(3) (85)
5	DIB (1.1)	0	120; 40	No reaction
6	TFIB (1.1)	1.0	30; 40	(3) (100)
7	Iodosylbenzene (1.6)	1.0	120; 40	(3) (89)
8	o-Iodosylbenzoic acid (1.1)	1.0	180; reflux	No reaction
9	Iodylbenzene (2.2)	2.0	120; 45	(1) (20), (2) (70)

[a] In cyclohexane and under irradiation with two 100-W tungsten-filament lamps.

Table 2. Reaction of steroidal alcohols with DIB–iodine reagent[a]

Entry	Alcohol	DIB (mmol)	Iodine (mmol)	Conditions (min; °C)	Products (yield %)
1	(4)	2.0	1.5	60; 20	(6) (32)
2	(4)	2.0	1.5	240; 8—10	(6) (62)[b]
3	(8)	2.2	1.6	180; 35	(10) (19), (11) (7) (12) (38), (13) (11)
4	(8)	4.2	2.6	300; 25	(11) (17), (13) (11) (14) (19), (17) (8)
5	(19)	1.1	1.0	30; 35	(20) (61)
6	(21)	1.1	1.0	30; 25	(22) (53)
7	(25)	1.1	0.5	40; 40	(26) (92)
8	(25)	2.0	0.3	90; 40	(26) (90)
9	(25)	1.1	0.2	150; 40	(26) (80), (25) (10)

[a] In cyclohexane under irradiation with two 100-W tungsten-lamps.
[b] The reaction crude was treated with silver acetate in acetone.

presence of iodine is necessary for the reaction to take place (entry 5) but when only 0.3 mol equiv. was used the yield did not decrease significantly, although longer times were needed (Table 1, compare entries 3 and 4). A better yield of tetra-hydrofuran derivative (3) was achieved with TFIB under very mild conditions using stoicheiometric quantities of reagent and iodine (Table 1, entry 6). The best yield reported in the functionlization of the 19-metal group from a 6β-alcohol was 84% using LTA and iodine.[8]

Other examples of this reaction employing the commercially available organoiodine reagent DIB and several steroidal alcohols are shown in Table 2. The photolysis of 5α-cholestan-2β-ol (4) gave the 2β,19-epoxy compound (6) (Table 2, entries 1 and 2). The formation of the iodohydrin (5) could be observed by t.l.c. but we were unable to isolate it in pure state. When the reaction crude was treated with silver acetate in acetone the chemical yield of epoxide (6) was notably increased (Table 2, entry 2).
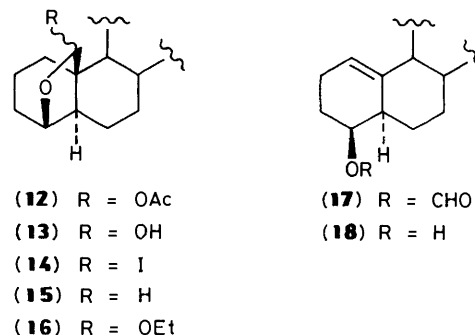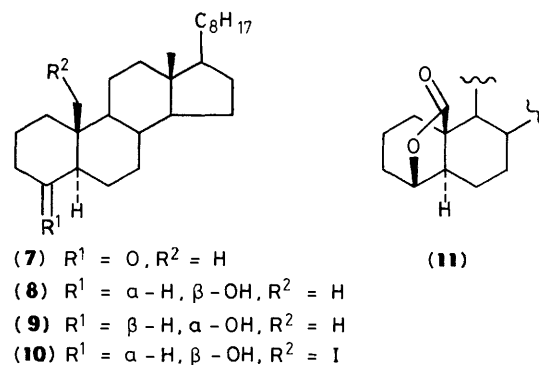
The structure of compound (6) was determined on the basis of spectral evidence. Its ^{1}H n.m.r. spectrum shows an AB system at δ_H 3.64 and 3.81 (J 8 Hz) for the two protons at C-19. The ^{13}C n.m.r. spectrum (DEPT experiment) displays the C-19 signal at δ_C 67.62 and the molecular composition is in agreement with an accurate mass spectrometric measurement. In contrast with the results obtained with LTA, no products arising from a second hydrogen-abstraction reaction were detected under these conditions.[9]

The functionalization of the steroidal methyl group at C-10

from an alkoxyl radical at C-4 gave rise to a more complex reaction. Thus, photolysis of alcohol (8) using 2.2 mmol of DIB per mmol of alcohol (Table 2, entry 3) gave a mixture of iodo-hydrin (10), lactone (11), hemiacetal acetate (12), and lactol (13).

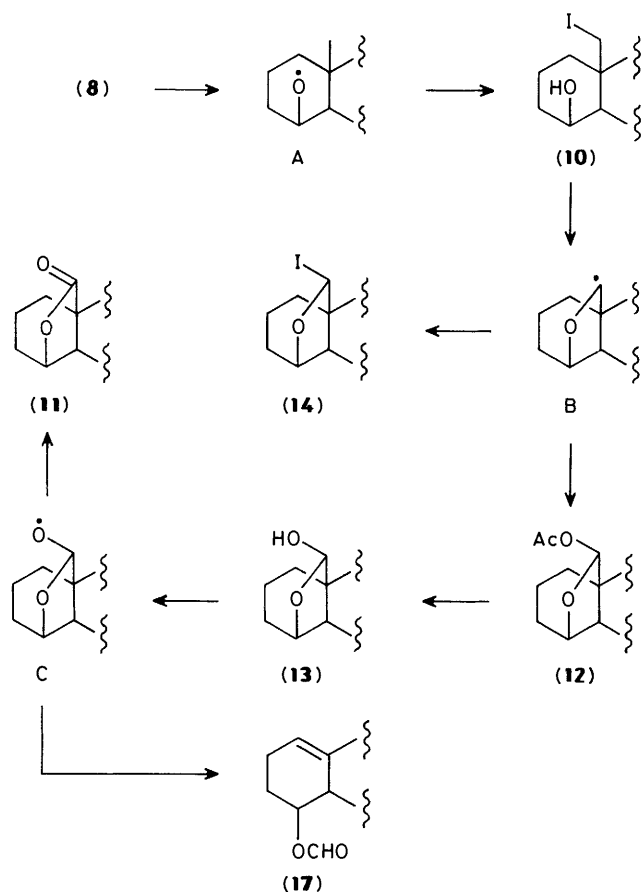The examination of the ^{1}H n.m.r. spectra of compounds (12) and (13) revealed that they are mixtures of 19R and 19S isomers. The structure of iodohydrin (10) was confirmed by means of ^{1}H n.m.r. and ^{13}C n.m.r. data. In particular an AB system was observed at δ_H 3.57 and 4.45 for the two protons at C-19 and also the chemical shift for this carbon at δ_C 11.64.

The mixture of lactols (13) was transformed with Jones reagent into lactone (11), identical with that obtained by photolysis of compound (8). Treatment of lactol (13) in ethanol with traces of hydrochloric acid gave a mixture (70:30) of the ethyl acetals (19S)-(16) and (19R)-(16) which were separated by chromatography. The ethyl acetal structure of these compounds was made evident by ^{1}H n.m.r. spectroscopy and the C-19 stereochemistry was tentatively assigned on a steric basis.

(7) R^1 = O, R^2 = H
(8) R^1 = α-H, β-OH, R^2 = H
(9) R^1 = β-H, α-OH, R^2 = H
(10) R^1 = α-H, β-OH, R^2 = I

(11)

(12) R = OAc
(13) R = OH
(14) R = I
(15) R = H
(16) R = OEt

(17) R = CHO
(18) R = H

When the photolysis of the alcohol (8) was realized with larger amounts of reagents and longer reaction times, in addition to the mixture of lactols (13) and the lactone (11), two new compounds were obtained: the iodo compound (14) and the formate derivative (17) (Table 2, entry 4). The spectroscopic data were fully compatible with the structure proposed for these compounds. Thus a singlet at δ_H 5.60 is observed for the proton at C-19 in the ^{1}H n.m.r. spectrum of compound (14), the chemical shift for this carbon being at δ_C 104.52 in its ^{13}C n.m.r. spectrum. This iodo compound (14) was very stable and no reaction was observed when it was treated with silver acetate, sodium acetate, sodium hydroxide, or tributyltin hydride–azoisobutyronitrile under several conditions. However, the reaction of iodide (14) with an excess of zinc in acetic acid at reflux temperature gave a mixture of the ether (15) and hemiacetal acetate (12).

The formate (17) can be hydrolysed to the alcohol (18) with loss of one carbon atom as demonstrated by high-resolution mass spectrometry; other additional spectroscopic data are

(8) → A → **(10)**

(11) **(14)** B

(19) R¹ = R² = H, R³ = OH
(20) R¹ = I, R² = H, R³ = OH
(21) R¹ = R³ = H, R² = OH
(22) R¹ = I, R² = OH, R³ = H

(23) R¹ = Me, R² = H
(24) R¹ = H, R² = Me

C **(13)** **(12)**

(17)

(25) **(26)**

Scheme.

entirely in accord with the proposed structure (see Experimental section).

A reaction mechanism that may explain the results obtained during the photolysis of alcohol **(8)** is summarized in the Scheme and is analogous to that proposed by Kalvoda et al.[2] The alkoxyl radical A initially formed can abstract a proton from the methyl group at C-10 to give the iodohydrin **(10)**. Hindered rotation of the axial CH_2I group facilitates a second hydrogen abstraction to give rise to the radical intermediate B which can trap iodine or the acetyl radical to give compounds **(14)** or **(12)** respectively. The alcohol **(13)**, formed in situ by hydrolysis of acetate **(12)**, reacts further with an excess of DIB to give the lactone **(11)** and the formate **(17)** through β-fragmentation of the radical C.

The functionalization of the C-13 methyl group in the pregnane series was achieved by photolysis of the 20R- and 20S-alcohols **(19)** and **(21)** (Table 2, entries 5 and 6). The reaction gave the iodohydrins **(20)** and **(22)** respectively, and no products resulting from double functionalization could be observed under these conditions, in contrast with the results obtained with other oxidants.[10] The evidence for the structure of these compounds may be summarized by the following n.m.r. spectral data: the absence of the C-13 methyl signal with concomitant introduction of an AB quartet for the two protons at C-18 and the strong shielding observed in the resonance of the carbon bearing the iodine atom in the ^{13}C n.m.r. spectrum. Both iodohydrins **(20)** and **(22)** yielded the respective tetrahydrofuran derivatives **(23)** and **(24)** when treated with silver acetate in acetone.

Another example of this reaction is the cyclization of dihydro-tigogenin 3-acetate **(25)** to give tigogenin acetate **(26)** in good
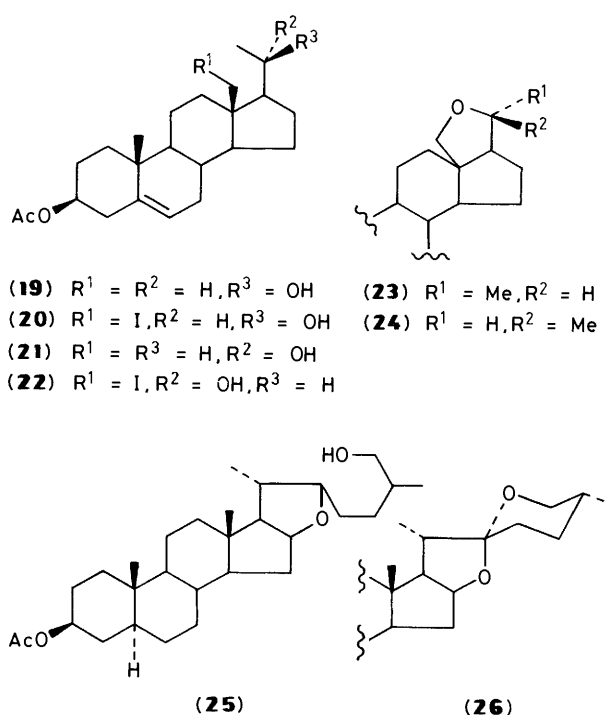
yield (Table 2, entries 7—9). In this case 0.3 mmol of iodine per mmol of substrate was used without significant loss of yield. However, 10% of starting material was recovered when only 0.2 mmol of iodine was used (entry 9).

In practice, the reactions proceed smoothly under mild conditions and the yields are usually better than those obtained with the heavy-metal derivative systems. It should be pointed out that in cases of single hydrogen abstraction only 1.1 mmol of DIB and 1 mmol of iodine are needed to complete the reaction, in contrast with the large excess of oxidant currently required with other methods.* These reagents also avoid some of the difficulties associated with the use of heavy-metal derivatives, such as toxicity and troublesome work-up procedures.

This methodology has been recently used by Baker[11] in the synthesis of a bis-spiroacetal model, the main structural feature of the polyether antibiotics salinomycin and narasin.

Experimental

M.p.s were determined with a Kofler hot-stage apparatus and are uncorrected. Optical rotations were measured at room temperature for solutions in $CHCl_3$ on a Perkin-Elmer 141 polarimeter. I.r. spectra were taken on a Perkin-Elmer 257 instrument for $CHCl_3$ solutions. ^1H N.m.r. spectra were recorded with a Perkin-Elmer R-12B (60 MHz), a R-32 (90 MHz), a Bruker AC80 (80 MHz), or a WP200SY (200 MHz) instrument and ^{13}C n.m.r. spectra on a Bruker AC80 (20.1 MHz) or WP200SY (50.3 MHz) for solutions in $CDCl_3$ with Me_4Si as internal reference. Low- and high-resolution mass spectra were determined with a VG Micromass ZAB-2F spectrometer at 70 eV. T.l.c. was performed on Merck silica gel 60 and column chromatography on Merck silica gel (0.063—0.2 mm). Circular layers of Merck silica gel 60 PF 254 (1 mm) were used on a Harrison Chromatotron for centrifugally assisted chromatography. The spray reagent for t.l.c. was vanillin (1 g) in H_2SO_4–EtOH (4:1; 200 ml).

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* For instance, although good results are generally observed when molar proportion of substrate:iodine:LTA are kept around 1:1.25:5, proportions of 1:5—20:5—30 are often reported.

The polyvalent iodine reagents (diacetoxyiodo)benzene (DIB) 98% and o-iodosylbenzoic acid were purchased from Aldrich and Sigma respectively. (Bistrifluoroacetoxyiodo)-benzene (TFIB),[12] iodosylbenzene,[13] and iodylbenzene[14] were prepared according to previously reported procedures.

Tetrabutylammonium Diacetoxyiodate(I).—Prepared following the procedure described for the preparation of the tetraethylammonium derivative.[15] To a solution of tetrabutylammonium iodide (1.44 g, 3.9 mmol) in dry chloroform (5 ml) was added DIB (1.25 g, 3.9 mmol) and the mixture was stirred overnight. After addition of dry ether the mixture was cooled to $-20\,°C$ and the brown crystalline products were filtered off, washed with dry ether, and dried *in vacuo* over P_2O_5 to yield the title compound (1.6 g, 85%), m.p. 66—68 °C (from $CHCl_3$–ether); δ_H(80 MHz) 1.02 (12 H, t, *J* 6 Hz, Me), 1.97 (6 H, s, OAc), and 3.35 (8 H, m, $w_{\frac{1}{2}}$ 20 Hz, NCH_2).

6β,19-*Epoxy-5α-cholestan-3β-yl Acetate* (3).—A solution of 5α-cholestane-3β,6β-diol 3-acetate (1) {m.p. 158.5—159.5 °C (from MeOH); $[\alpha]_D$ $-8°$ (*c* 0.242) (lit.,[16] m.p. 143—144 °C; $[\alpha]_D$ $-6°$), previously obtained by sodium borohydride reduction of 6-oxo-5α-cholestan-3β-yl acetate (2)} (50 mg, 0.11 mmol) in cyclohexane (10 ml) containing DIB (40 mg, 0.12 mmol) and iodine (28 mg, 0.11 mmol) was irradiated with two 100-W tungsten-filament lamps for 50 min at 40 °C. The reaction mixture was then poured into water and extracted with diethyl ether. The organic layer was washed successively with aqueous sodium thiosulphate and water. Silica gel column chromatography of the residue (hexane–ethyl acetate; 9:1) gave 6β,19-epoxy-5α-cholestan-3β-yl acetate (3) (45 mg, 90%), m.p. 114—115 °C (from MeOH) (lit.,[17] m.p. 114—116 °C); $\nu_{max.}$ 1 720, 1 250, and 1 030 cm⁻¹; δ_H (200 MHz) 0.68 (3 H, s, 13-Me), 0.83 (6 H, d, *J* 7 Hz, 25-Me₂), 0.86 (3 H, d, *J* 7 Hz, 20-Me), 2.00 (3 H, s, OAc), 3.69 (2 H, s, 19-H₂), 3.93 (1 H, m, $w_{\frac{1}{2}}$ 8 Hz, 6α-H), and 4.6 (1 H, m, $w_{\frac{1}{2}}$ 22 Hz, 3α-H); δ_C (50.3 MHz) 12.58 (C-18), 18.77 (C-21), 21.53 (*Me*CO), 22.70 (C-26), 22.78 (C-11), 22.94 (C-27), 23.76 (C-15), 23.98 (C-23), 26.65 (C-4), 27.72 (C-2), 28.16 (C-25), 28.43 (C-16), 32.07 (C-1), 34.82 (C-8), 35.92 (C-20), 36.33 (C-22), 37.65 (C-7), 39.66 (C-24), 40.14 (C-12), 43.36 (C-10), 44.04 (C-13), 50.98 (C-5), 54.38 (C-9), 55.52 (C-14), 56.37 (C-17), 69.02 (C-19), 72.34 (C-3), 81.20 (C-6), and 170.79 (Me*C*O); *m/z* 444.3615 (5%, M^+. Calc. for $C_{29}H_{48}O_3$: *M*, 444.3603), 384 (90, M^+ − AcOH), 369 (19), 366 (20), 271 (35), and 121 (100). The reactions of alcohol (1) with tetrabutylammonium diacetoxyiodate(I), TFIB, iodosylbenzene, o-iodosylbenzoic acid, and iodylbenzene have been performed analogously under the conditions shown in Table 1.

2β,19-*Epoxy-5α-cholestane* (6).—A solution of 5α-cholestan-2β-ol (4) (100 mg, 0.26 mmol) in cyclohexane (20 ml) containing DIB (170 mg, 0.53 mmol) and iodine (100 mg, 0.39 mmol) was irradiated as described previously at room temperature for 1 h. Usual work-up and chromatography of the residue (hexane–ethyl acetate; 95:5) gave the *ether* (6) (32 mg, 32%), m.p. 91—92.5 °C (from MeOH); $[\alpha]_D$ $+37°$ (*c* 0.16); δ_H(200 MHz) 0.61 (3 H, s, 13-Me), 0.85 (6 H, d, *J* 6.4 Hz, 25-Me₂), 0.89 (3 H, d, *J* 6.7 Hz, 20-Me), 3.64 and 3.81 (2 H, AB *J* 8.0 Hz, 19-H₂), and 4.25 (1 H, apparent t, 2α-H); δ_C(20.1 MHz) 11.83 (C-18), 18.70 (C-21), 21.02 (C-11), 22.53 (C-26), 22.76 (C-27), 23.85 (C-15), 24.16 (C-23), 27.19 (C-6), 27.99 (C-25), 28.18 (C-16), 30.57 (C-4 or -3), 31.57 (C-3 or -4), 32.01 (C-7), 35.75 (C-20), 36.19 (C-22), 38.61 (C-8), 39.53 (C-24), 39.75 (C-12 or -1), 41.26 (C-1 or -12), 42.32 (C-13), 43.80 (C-5), 46.55 (C-9), 47.34 (C-10), 56.32 (C-17), 56.74 (C-14), 67.62 (C-19), and 75.16 (C-2); *m/z* 386.3550 (42%, M^+. $C_{27}H_{46}O$ requires *M*, 386.3549), 371.3319 (1. $C_{26}H_{43}O$ requires, *m/z*, 371.3314), 356.3430 (12. $C_{26}H_{44}$ requires *m/z*, 356.3443), 301.2528 (5. $C_{21}H_{33}O$ requires *m/z*, 301.2531),

231.1758 (27. $C_{16}H_{23}O$ requires *m/z*, 231.1749), and 201.1660 (52. $C_{15}H_{21}O$ requires *m/z*, 201.1643). When the reaction was realized at 8—10 °C for 4 h, and the crude reaction mixture was treated with silver acetate (230 mg) in acetone (10 ml) for 2 h at room temperature, a better yield of the ether (6) was obtained (62 mg, 62%).

5α-*Cholestan-4β-ol* (8).—To a solution of 5α-cholestan-4-one (7) {m.p. 99—101 °C (from MeOH); $[\alpha]_D$ $+30°$ (*c* 0.312) (lit.,[18] 99—100 °C; $[\alpha]_D$ $+31°$) prepared by hydroboration and subsequent oxidation of cholest-4-ene} (1.5 g) in ethanol (150 ml), was added sodium borohydride (0.7 g) and the mixture was stirred at ambient temperature for 1.5 h. Work-up as usual gave a mixture of 5α-cholestan-4β-ol (8) (1.21 g) and 5α-cholestan-4α-ol (9) (0.27 g) which was separated by column chromatography (benzene–ethyl acetate; 97:3). The alcohol (8), m.p. 128—130 °C (from acetone); $[\alpha]_D$ $+30°$ (*c* 0.28) (lit.,[19] m.p. 132 °C; $[\alpha]_D$ $+29°$); $\nu_{max.}$ 3 610 cm⁻¹; δ_H(200 MHz) 0.62 (3 H, s, 13-Me), 0.84 (6 H, d, *J* 7 Hz, 25-Me₂), 0.88 (3 H, d, *J* 6.7 Hz, 20-Me), 1.00 (3 H, s, 10-Me), and 3.77 (1 H, m, $w_{\frac{1}{2}}$ 10 Hz, 4α-H); *m/z* 388 (M^+, 52%), 373 (36), 370 (30), 355 (26), 233 (100), 215 (77), and 201 (18). The alcohol (9), m.p. 186—188 °C (from acetone); $[\alpha]_D$ $+5°$ (*c* 0.291) (lit.,[19] m.p. 189 °C; $[\alpha]_D$ $+4°$); $\nu_{max.}$ 3 605 cm⁻¹; δ_H(200 MHz) 0.62 (3 H, s, 13-Me), 0.77 (3 H, s, 10-Me), 0.84 (6 H, d, *J* 6.6 Hz, 25-Me₂), 0.87 (3 H, d, *J* 6.7 Hz, 20-Me), and 3.42 (1 H, m, $w_{\frac{1}{2}}$ 30 Hz, 4α-H); *m/z* 388 (M^+, 49%), 373 (37), 370 (25), 355 (14), 233 (100), 215 (65), and 201 (11).

Reaction of 5α-*Cholestan-4β-ol* (8) *with DIB–I₂*.—(*a*) A solution of 5α-cholestan-4β-ol (8) (93 mg, 0.24 mmol) in cyclohexane (30 ml) containing DIB (170 mg, 0.53 mmol) and iodine (100 mg, 0.39 mmol) was irradiated, as described previously, at 35 °C for 3 h. Usual work-up gave a mixture of 19-*iodo-5α-cholestan-4β-ol* (10) (25 mg, 19%), 5α-*cholestan-*19,4-*lactone* (11) (7.3 mg, 7%), *hemiacetal acetate* (12) (43 mg, 38%), and *lactol* (13) (11 mg, 11%) which was separated by chromatography (benzene–ethyl acetate; 99:1). The iodo alcohol (10), amorphous; $\nu_{max.}$ 3 600 cm⁻¹; δ_H(200 MHz) 0.71 (3 H, s, 13-Me), 0.86 (6 H, d, *J* 6.5 Hz, 25-Me₂), 0.89 (3 H, d, *J* 6.4 Hz, 20-Me), 3.57 and 4.45 (2 H, AB, *J* 11 Hz, 19-H₂), and 3.86 (1 H, br s, 4α-H); δ_C(50.3 MHz) 11.64 (C-19), 12.34 (C-18), 16.83, 18.78 (C-21), 22.36, 22.72 (C-26), 22.96 (C-27), 24.01, 24.35 (C-23), 26.19, 28.18 (C-25), 28.35, 32.38, 34.19, 35.94 (C-20), 36.01, 36.35 (C-22), 37.47 (C-10), 39.70 (C-24), 39.75, 40.48, 42.71 (C-13), 50.06, 56.31 (C-17), 56.63 (C-14), 57.12 and 72.30 (C-3); *m/z* 514.2681 ($<1\%$, M^+. $C_{27}H_{47}IO$ requires *M*, 514.2673), 496.2578 (2%, M^+ − H_2O. $C_{27}H_{45}I$ requires *m/z* 496.2568), 386.3522 (28, *M* − HI. $C_{27}H_{46}O$ requires *m/z* 386.3549), and 369.3501 (44. $C_{27}H_{45}$ requires *m/z*, 369.3521).

The lactone (11), m.p. 161—163 °C (from MeOH), $[\alpha]_D$ $+5°$ (*c* 0.328); $\nu_{max.}$ 1 760 cm⁻¹; δ_H(200 MHz) 0.70 (3 H, s, 13-Me), 0.83 (6 H, d, *J* 6.6 Hz, 25-Me₂), 0.88 (3 H, d, *J* 6.9 Hz, 20-Me), and 4.22 (1 H, m, $w_{\frac{1}{2}}$ 10 Hz, 4α-H); δ_C(50.3 MHz) 12.07 (C-18), 18.81 (C-2), 18.89 (C-21), 20.71 (C-11), 22.72 (C-26), 22.96 (C-27), 24.01 (C-23), 24.30 (C-15), 27.21 (C-7), 27.96 (C-6), 28.18 (C-25), 28.35 (C-16), 29.81 (C-1), 31.73 (C-3), 35.89 (C-20), 36.38 (C-22), 37.73 (C-8), 39.70 (C-24), 40.27 (C-12), 42.80 (C-13), 46.86 (C-9), 49.32 (C-10), 50.98 (C-5), 56.05 (C-14), 56.46 (C-17), 79.97 (C-4), and 178.55 (C-19); *m/z* 400.3353 (48%, M^+. $C_{27}H_{44}O_2$ requires *M*, 400.3341), 385 (4), 372 (3), 356 (15), 355 (22), 246 (53), 245 (52), and 101 (100).

Compound (12), amorphous, was a mixture 80:20 of two isomeric hemiacetal acetates as determined by ¹H n.m.r.; $\nu_{max.}$ 1 730 and 1 240 cm⁻¹; δ_H(200 MHz) 0.63 and 0.66 (3 H, each s, 13-Me), 0.83 (6 H, d, *J* 6.4 Hz, 25-Me₂), 0.86 (3 H, d, *J* 5.6 Hz, 20-Me), 2.11 and 2.12 (3 H, each s, OAc), 4.18 and 3.98 (1 H, each m, $w_{\frac{1}{2}}$ 10 Hz, 4α-H), and 5.92 and 6.26 (1 H, each s, 19-H); *m/z* 444.3595 (1%, M^+. $C_{29}H_{48}O_3$ requires *M*, 444.3603),

401.3417 (3. $C_{27}H_{45}O_2$ requires m/z, 401.3420), 384.3363 (35. $C_{27}H_{44}O$ requires m/z 384.3392), 356.3405 (100. $C_{26}H_{44}$ requires m/z, 356.3443), 341.3185 (29. $C_{25}H_{41}$ requires m/z, 341.3208), and 343.2103 (1. $C_{18}H_{27}$ requires m/z, 243.2112).

Compound (13), amorphous, was a 60:40 mixture of two lactols as determined by ^{1}H n.m.r.; $v_{max.}$ 3 600 cm^{-1}; δ_H(200 MHz) 0.64 and 0.67 (3 H, each s, 13-Me), 0.83 (6 H, d, J 6.5 Hz, 25-Me$_2$), 0.86 (3 H, d, J 6.4 Hz, 20-Me), 3.91 and 4.13 (1 H, each d, J 10 Hz, 4α-H), and 5.57 and 5.11 (1 H, each m, $w_{\frac{1}{2}}$ 10 Hz, 19-H); m/z 402.3501 (1%, M^+. $C_{27}H_{46}O_2$ requires M, 402.3498), 400.3400 (4. $C_{27}H_{44}O_2$ requires m/z, 400.3342), 356. 3390 (100. $C_{26}H_{44}$ requires m/z, 356.3443), 341.3215 (65. $C_{25}H_{41}$ requires m/z, 341.3208), 343.3248 (71. $C_{25}H_{43}$ requires m/z, 343.3364), 217.1921 (46. $C_{16}H_{25}$ requires m/z, 217.1956), and 201 (87).

Oxidation of this lactol mixture (13) with Jones reagent yielded the lactone (11), identical with that previously prepared. Reaction of compound (13) (20 mg) in ethanol (5 ml) containing traces of hydrochloric acid at ambient temperature for 1 h gave a mixture of the ethyl acetals (19S)-(16) (13 mg) and (19R)-(16) (6 mg) which were separated by chromatography (hexane–ethyl acetate; 98:2). Compound (19S)-(16), amorphous, δ_H(200 MHz) 0.67 (3 H, s, 13-Me), 0.84 (6 H, d, J 6.7 Hz, 25-Me$_2$), 0.87 (3 H, d, J 6.9 Hz, 20-Me), 1.21 (3 H, t, J 7 Hz, OCH$_2$$Me$), 3.35 and 3.82 (2 H, each m, $w_{\frac{1}{2}}$ 19 Hz, OCH_2Me), 4.06 (1 H, m, $w_{\frac{1}{2}}$ 10 Hz, 4α-H), and 4.68 (1 H, s, 19-H); irradiation at δ 1.21 give rise to a AB system at δ 3.43 and 3.89 (J 9.7 Hz); m/z 385 (4%, M^+ − OEt), 384 (3), 369 (5), 356 (100), 353 (10), 341 (37), 243 (40), 217 (12), and 201 (46). Compound (19R)-(16), amorphous, δ_H(200 MHz) 0.64 (3 H, s, 13-Me), 0.84 (6 H, d, J 6.7 Hz, 25-Me$_2$), 0.87 (3 H, d, J 7 Hz, 20-Me), 1.21 (3 H, t, J 7 Hz, OCH$_2$$Me$), 3.51 and 3.80 (2 H, each m, $w_{\frac{1}{2}}$ 19 Hz, OCH_2Me), 3.88 (1 H, m, $w_{\frac{1}{2}}$ 10 Hz, 4α-H), and 5.16 (1 H, s, 19-H); m/z 385 (1%, M^+ − OEt), 384 (1), 356 (100), 343 (49), 341 (44), 217 (29), and 201 (50).

(*b*) A solution of 5α-cholestan-4β-ol (8) (410 mg, 1.05 mmol) in cyclohexane (50 ml) containing DIB (680 mg, 2.1 mmol) and iodine (400 mg, 1.57 mmol) was irradiated at 25 °C for 3 h. Then DIB (680 mg, 2.1 mmol) and iodine (254 mg, 1 mmol) were added in two portions every hour. Usual work-up gave a mixture of 5α-cholestan-19,4β-lactone (11) (70 mg, 17%), the lactol (13) (46 mg, 11%), (19R)-4β-19-*epoxy-19-iodo*-5α-*cholestane* (14) (104 mg, 19%), and *formate* (17) (34 mg, 8%) which was separated by chromatography (hexane–ethyl acetate; 98:2). The iodo compound (14), m.p. 230—233 °C (from CHCl$_3$–MeOH); [α]$_D$ +96° (*c* 0.304); δ_H(200 MHz) 0.67 (3 H, s, 13-Me), 0.83 (6 H, d, J 6.6 Hz, 25-Me$_2$), 0.86 (3 H, d, J 6.7 Hz, 20-Me), 3.84 (1 H, m, $w_{\frac{1}{2}}$ 10 Hz, 4α-H), and 5.60 (1 H, s, 19-H); δ_C (50.3 MHz) 12.39 (C-18), 18.89 (C-2), 18.89 (C-21), 22.73 (C-26), 22.98 (C-27), 23.06 (C-11), 24.04 (C-23), 24.37 (C-15), 26.92 (C-6), 28.19 (C-25), 28.41 (C-16), 30.24 (C-1), 31.73 (C-7), 33.00 (C-3), 35.90 (C-20), 36.38 (C-22), 36.70 (C-7), 39.72 (C-24), 40.89 (C-12), 43.03 (C-13), 47.01 (C-10), 48.56 (C-9), 52.58 (C-5), 56.25 (C-17), 56.60 (C-14), 81.14 (C-4), and 104.52 (C-19); m/z 512.2530 (<1%, M^+. $C_{27}H_{45}IO$ requires M, 512.2517), 385.3449 (100, M − I. $C_{27}H_{45}O$ requires m/z, 358.3468), 367 (20), 355 (19), 341 (8), and 201 (19).

The formate (17), m.p. 90—92 °C (from MeOH); [α]$_D$ −68 °C (*c* 0.096); $v_{max.}$ 1 710 cm^{-1}; δ_H(200 MHz) 0.64 (3 H, s, 13-Me), 0.84 (6 H, d, J 6.9 Hz, 25-Me$_2$), 0.89 (3 H, d, J 6.4 Hz, 20-Me), 5.19 (1 H, m, $w_{\frac{1}{2}}$ 20 Hz, 4α-H), 5.34 (1 H, m, $w_{\frac{1}{2}}$ 10 Hz, 1-H), and 8.10 (1 H, s, OCHO); δ_C(50.3 MHz) 12.23 (C-18), 18.86 (C-21), 22.73 (C-26), 22.78 (C-2), 22.99 (C-27), 23.98 (C-11), 24.13 (C-23), 24.64 (C-15), 25.32 (C-3), 28.12 (C-6), 28.18 (C-25), 28.44 (C-16), 31.04 (C-7), 35.95 (C-20), 36.34 (C-22), 39.71 (C-24), 39.76 (C-12), 41.55 (C-8), 43.12 (C-13), 43.29 (C-9), 48.19 (C-5), 56.30 (C-17), 56.56 (C-14), 72.79 (C-4), 114.95 (C-1), 141.85 (C-10), and 161.02 (C-19); m/z 400.3362 (1%, M^+. $C_{27}H_{44}O_2$ requires M, 400.3341), 385 (0.8), 370 (0.7), 354 (100), 339 (6), 241

(21), and 199 (27). Saponification of compound (17) with methanolic potassium hydroxide (3%) at ambient temperature gave the alcohol (18), m.p. 111—112 °C (from MeOH); $v_{max.}$ 3 600 cm^{-1}; δ_H(200 MHz) 0.66 (3 H, s, 13-Me), 0.87 (6 H, d, J 6.6 Hz, 25-Me$_2$), 0.92 (3 H, d, J 6.5 Hz, 20-Me), 3.94 (1 H, m, $w_{\frac{1}{2}}$ 20 Hz, 4α-H), and 5.33 (1 H, m, $w_{\frac{1}{2}}$ 10 Hz, 1-H); m/z 372.3527 (4%, M^+. $C_{26}H_{44}O$ requires M, 372.3391), 370.3279 (13. $C_{26}H_{42}O$ requires m/z, 370.3234), 354.3316 (100. $C_{26}H_{42}$ requires, m/z, 354.3285), 260.2463 (4. $C_{19}H_{32}$ requires m/z, 260.2424), and 241.1931 (28. $C_{18}H_{25}$ requires m/z, 241.1907).

4β,19-*Epoxy-*5α-*cholestane* (15).—To a solution of compound (14) (28 mg) in glacial acetic acid (5 ml) was added zinc powder (360 mg) and the mixture was refluxed for 2.5 h, filtered, and the filtrate poured into water, neutralized with sodium hydrogen carbonate, and extracted with chloroform. After the extract had been dried over Na$_2$SO$_4$, the solvent was evaporated off and the residue was purified by chromatography (benzene) to afford compounds (15) (13 mg) and (12) (6 mg). *Compound* (15), m.p. 202—204 °C (from acetone); [α]$_D$ +45° (*c* 0.186); δ_H(200 MHz) 0.62 (3 H, s, 13-Me), 0.84 (6 H, d, J 6.3 Hz, 25-Me$_2$), 0.86 (3 H, d, J 5.1 Hz, 20-Me), 3.64 and 3.86 (2 H, AB, J 8.1 Hz, 19-H$_2$), and 3.89 (1 H, m, $w_{\frac{1}{2}}$ 5 Hz, 4α-H); δ_C (50.3 MHz) 12.36 (C-18), 18.84 (C-21), 19.58 (C-2), 22.72 (C-26), 22.98 (C-27), 23.95 (C-11), 24.03 (C-23), 24.25 (C-15), 26.89 (C-6), 28.18 (C-25), 28.42 (C-16), 29.80 (C-7), 32.82 (C-3), 35.94 (C-20), 36.36 (C-22), 36.36 (C-1), 36.69 (C-8), 39.70 (C-24), 40.55 (C-12), 43.05 (C-13), 46.13, (C-10), 48.22 (C-5), 51.61 (C-9), 55.91 (C-14), 56.66 (C-17), 71.43 (C-19), and 81.47 (C-4); m/z 386.3542 (36%, M^+. $C_{27}H_{46}O$ requires M, 386.3547), 371.3369 (5. $C_{26}H_{43}O$ requires m/z, 371.3312), 368.3422 (4. $C_{27}H_{44}$ requires m/z, 368.3440), 343 (25), 273.2203 (4. $C_{19}H_{29}O$ requires m/z, 273.2218), 255.2070 (5. $C_{19}H_{27}$ requires m/z, 255.2111), 246.1975 (21. $C_{17}H_{26}O$ requires, m/z, 246.1968), 232.1784 (50. $C_{16}H_{24}O$ requires m/z, 232.1826), 215.1769 (22. $C_{16}H_{23}$ requires m/z, 215.1799), and 201.1630 (100. $C_{15}H_{21}$ requires m/z 201.1642).

The amorphous compound (12) was a *ca.* 1:1 mixture of the two isomeric hemiacetal acetates, as determined by ^{1}H n.m.r., identical with those previously obtained.

Reduction of 3β-*Hydroxypregn*-5-*en*-20-*one Acetate.*—A solution of the title compound (1.4 g) in ethanol (200 ml) was hydrogenated in the presence of Raney Ni (30 g) at room temperature and atmospheric pressure for 77 h. The mixture was filtered and the filtrate was evaporated under reduced pressure to give a 1:1 mixture of the 20R-alcohol (19) (566 mg) and 20S-alcohol (21) (562 mg) which was separated by chromatography (benzene–ethyl acetate; 9:1). The 20R-alcohol (19), m.p. 163.5—165.5 °C (from MeOH); [α]$_D$ −74° (*c* 0.286) (lit.,[20] 164.5—165.5 °C; [α]$_D$ −68°); $v_{max.}$(KBr) 3 550, 1 720, 1 250, and 1 030 cm^{-1}; δ_H(90 MHz) 0.77 (3 H, s, 13-Me), 1.03 (3 H, s, 10-Me), 1.14 (3 H, d, J 7 Hz, 20-Me), 2.03 (3 H, s, OAc), 3.75 (1 H, m, $w_{\frac{1}{2}}$ 20 Hz, 20-H), 4.60 (1 H, m, $w_{\frac{1}{2}}$ 27 Hz, 3α-H), and 5.39 (1 H, m, $w_{\frac{1}{2}}$ 10 Hz, 6-H); δ_C(50.3 MHz) 12.44 (C-18), 19.43 (C-19), 21.01 (C-11), 21.52 (*Me*CO), 23.80 (C-21), 24.67 (C-15), 25.76 (C-16), 27.87 (C-2), 31.83 (C-8), 32.02 (C-7), 36.75 (C-10), 37.12 (C-1), 38.23 (C-4), 39.93 (C-12), 42.38 (C-13), 50.16 (C-9), 56.28 (C-14), 58.58 (C-17), 70.59 (C-20), 74.06 (C-3), 122.57 (C-6), 139.87 (C-5), and 170.61 (Me*C*O); m/z 300 (M^+ − AcOH, 100%), 285 (17), 282 (23), and 255 (7).

The 20S-alcohol (21), m.p. 139—141 °C (from MeOH); [α]$_D$ −62° (*c* 0.21) (lit.,[20] 142—143 °C; [α]$_D$ −56°); $v_{max.}$ 3 370, 1 720, 1 250, and 1 030 cm^{-1}; δ_H(200 MHz) 0.68 (3 H, s, 13-Me), 1.03 (3 H, s, 10-Me), 1.23 (3 H, d, J 7 Hz, 20-Me), 2.03 (3 H, s, OAc), 3.74 (1 H, m, $w_{\frac{1}{2}}$ 20 Hz, 20-H), 4.60 (1 H, m, $w_{\frac{1}{2}}$ 27 Hz, 3α-H), and 5.39 (1 H, m, $w_{\frac{1}{2}}$ 10 Hz, 6-H); δ_C(50.3 MHz) 12.57 (C-18), 19.43 (C-19), 20.88 (C-11), 21.54 (*Me*CO), 23.67 (C-21), 24.32 (C-15), 25.79 (C-16), 27.89 (C-2), 31.65 (C-8), 31.98 (C-7), 36.74 (C-10),

37.13 (C-1), 38.23 (C-4), 38.88 (C-12), 41.72 (C-13), 50.13 (C-9), 56.63 (C-14), 58.53 (C-17), 70.34 (C-20), 74.05 (C-3), 122.64 (C-6), 139.79 (C-5), and 170.62 (MeCO); m/z 300 (M^+ − AcOH, 100%), 285 (13), 282 (28), and 255 (10).

(20R)-18-*Iodopregn-5-ene*-3β,20-*diol*   3-*Acetate*   (20).—A solution of (20R)-pregn-5-ene-3β,20-diol 3-acetate (19) (200 mg, 0.55 mmol) in cyclohexane (20 ml) containing DIB (195 mg, 0.6 mmol) and iodine (140 mg, 0.55 mmol) was irradiated with two 100-W filament lamps for 30 min at 35 °C. Work-up as described previously gave a residue, which was subjected to chromatography (benzene–ethyl acetate; 97:3) to give the (20R)-18-*iodopregn-5-ene*-3β,20-*diol* 3-*acetate* (20) (165 mg, 61%), amorphous; $\nu_{max.}$ 3 540, 1 720, 1 250, and 1 030 cm^{-1}; δ_H(200 MHz) 0.99 (3 H, s, 13-Me), 1.10 (3 H, d, J 6 Hz, 20-Me), 2.00 (3 H, s, OAc), 3.12 and 3.28 (2 H, AB, J 10.6 Hz, 18-H$_2$), 4.00 (1 H, m, $w_{\frac{1}{2}}$ 20 Hz, 20-H), 4.6 (1 H, m, $w_{\frac{1}{2}}$ 27 Hz, 3α-H), and 5.3 (1 H, m, $w_{\frac{1}{2}}$ 10 Hz, 6-H); δ_C(50.3 MHz) 10.81 (C-18), 19.42 (C-19), 20.53 (C-11), 21.53 (MeCO), 22.42 (C-21), 24.51 (C-15), 25.46 (C-16), 27.81 (C-2), 31.82 (C-7), 32.43 (C-8), 36.71 (C-10), 37.03 (C-1), 38.19 (C-4), 40.38 (C-12), 44.31 (C-13), 49.79 (C-9), 56.29 (C-14), 58.74 (C-17), 69.42 (C-20), 73.91 (C-3), 122.06 (C-6), 140.02 (C-5), and 170.61 (MeCO); m/z 486.1628 ($<$1%, M^+. $C_{23}H_{35}IO_3$ requires M, 486.1634), 426.1432 (6, M − AcOH. $C_{21}H_{31}IO$ requires m/z, 426.1420), 408 (2), 340 (13), 298.2305 (100. $C_{21}H_{30}O$ requires m/z, 298.2299), 283 (9), 280 (50), 265 (27), and 253 (11).

(20R)-18,20-*Epoxypregn-5-en*-3β-*yl*   Acetate   (23).—To a solution of (20R)-18-iodopregn-5-ene-3β,20-diol 3-acetate (20) (25 mg) in acetone (5 ml) was added silver acetate (35 mg). The mixture was stirred at room temperature in the dark for 30 h. Evaporation of the filtrate and chromatography of the residue (benzene–ethyl acetate; 9:1) gave (20R)-18,20-epoxypregn-5-en-3β-yl acetate (23) (16.5 mg, 90%), m.p. 133—135 °C (from MeOH) (lit.,[21] 134 °C); $\nu_{max.}$ 1 720, 1 250, and 1 030 cm^{-1}; δ_H(200 MHz) 0.93 (3 H, s, 13-Me), 1.19 (3 H, d, J 6 Hz, 20-Me), 2.00 (3 H, s, OAc), 3.43 and 3.70 (2 H, AB, J 9.3 Hz, 18-H$_2$), 3.7 (1 H, m, 20-H), 4.6 (1 H, m, $w_{\frac{1}{2}}$ 27 Hz, 3α-H), and 5.3 (1 H, m, $w_{\frac{1}{2}}$ 10 Hz, 6-H); δ_C(50.3 MHz) 19.48 (C-19), 21.55 (C-21), 21.55 (MeCO), 23.22 (C-11), 26.27 (C-15), 27.90 (C-2), 32.29 (C-16), 32.29 (C-7), 33.65 (C-8), 36.78 (C-10), 36.97 (C-12), 37.14 (C-1), 38.26 (C-4), 49.75 (C-9), 55.19 (C-13), 55.19 (C-17), 55.48 (C-14) 71.64 (C-18), 73.99 (C-3), 84.57 (C-20), 122.38 (C-6), 139.83 (C-5), and 170.65 (MeCO); m/z 298.2283 (100%, M^+ − AcOH. Calc. for $C_{21}H_{30}O$: m/z, 298.2296) and 283 (20).

(20S)-19-*Iodopregn-5-ene*-3β,20-*diol*   3-*Acetate*   (22).—A solution of (20S)-pregn-5-ene-3β,20-diol 3-acetate (21) (118 mg, 0.33 mmol) in cyclohexane (11 ml) containing DIB (115.8 mg, 0.36 mmol) and iodine (84 mg, 0.33 mmol) and irradiated with two 100-W tungsten-filament lamps for 30 min at 25 °C. Work-up as described previously gave a residue, which was subjected to chromatography (benzene–ethyl acetate; 9:1). The (20S)-18-iodopregn-5-ene-3β-20-diol 3-acetate (22) obtained as an oil (84 mg, 53%) possessed the following properties: $\nu_{max.}$ 1 720, 1 250, and 1 030 cm^{-1}; δ_H(200 MHz) 0.99 (3 H, s, 10-Me), 1.27 (3 H, d, J 6 Hz, 20-Me), 2.00 (3 H, s, OAc), 3.21 and 3.28 (2 H, AB, J 19 Hz, 18-H$_2$), 4.2 (1 H, m, $w_{\frac{1}{2}}$ 17 Hz, 20-H), 4.6 (1 H, m, $w_{\frac{1}{2}}$ 27 Hz, 3α-H), and 5.3 (1 H, m, $w_{\frac{1}{2}}$ 10 Hz, 6-H); δ_C(50.3 MHz) 11.91 (C-18), 19.43 (C-19), 20.47 (C-11), 21.55 (MeCO), 22.60 (C-16), 24.28 (C-15), 24.56 (C-21), 27.86 (C-2), 31.87 (C-7), 32.19 (C-8), 36.79 (C-10), 37.08 (C-1), 38.21 (C-4), 39.56 (C-12), 43.32 (C-13), 50.02 (C-9), 56.63 (C-14), 58.26 (C-17), 65.95 (C-20), 73.95 (C-3), 122.19 (C-6), 140.03 (C-5), and 170.65 (MeCO); m/z 486.1548 ($<$1%, M^+. $C_{23}H_{35}IO_3$ requires M, 486.1633), 426.1385 (5, M − AcOH. $C_{21}H_{31}IO$ requires m/z 426.1421), 408.1239 (2. $C_{21}H_{29}I$ requires m/z 408.1316) 298.2272 (100. $C_{21}H_{30}O$

requires m/z, 298.2297), 283.2111 (13. $C_{20}H_{27}O$ requires m/z, 283.2062), 280.2194 (7. $C_{21}H_{28}$ requires m/z, 280.2191), and 253 (9).

(20S)-18,20-*Epoxypregn-5-en*-3β-*yl*   Acetate   (24).—To a solution of (20S)-18-iodopregn-5-ene-3β,20-diol 3-acetate (22) (25 mg) in acetone (5 ml) was added silver acetate (35 mg) and the mixture was stirred at room temperature in the dark for 20 h. Work-up as described previously gave (20S)-18,20-*epoxypregn-5-en*-3β-*yl acetate* (24) (17.2 mg, 93%), m.p. 164—166 °C (from MeOH); $\nu_{max.}$ 1 720, 1 250, and 1 030 cm^{-1}; δ_H(200 MHz) 0.92 (3 H, s, 13-Me), 1.18 (3 H, d, J 6 Hz, 20-Me), 2.00 (3 H, s, OAc), 3.39 and 3.67 (2 H, AB, J 9.1 Hz, 18-H$_2$), 3.9 (1 H, m, $w_{\frac{1}{2}}$ 18 Hz, 20-H), 4.6 (1 H, m, $w_{\frac{1}{2}}$ 27 Hz, H$_2$), and 5.35 (1 H, m, $w_{\frac{1}{2}}$ 10 Hz, 6-H); δ_C(50.3 MHz) 16.27 (C-21), 19.50 (C-19), 21.56 (MeCO), 22.48 (C-11), 23.44 (C-15), 27.07 (C-16), 27.91 (C-2), 32.14 (C-7), 34.01 (C-8), 36.63 (C-12), 36.77 (C-10), 37.22 (C-1), 38.26 (C-4), 49.79 (C-9), 52.97 (C-17), 55.03 (C-13), 55.58 (C-14), 73.57 (C-18), 74.03 (C-3), 76.90 (C-20), 122.52 (C-6), 139.75 (C-5), and 170.69 (MeCO); m/z 358.2500 ($<$1%, M^+. $C_{23}H_{34}O_3$ requires M, 358.2508), 298.2233 (100, M − AcOH. $C_{21}H_{30}O$ requires m/z, 298.2296), and 283 (6).

Tigogenin Acetate (26).—A solution of dihydrotigogenin 3-acetate (25) (100 mg, 0.22 mmol) in cyclohexane (20 ml) containing DIB (78 mg, 0.24 mmol) and iodine (27.6 mg, 0.11 mmol) was irradiated for 40 min at 40 °C as described previously. After work-up, the residue was purified by chromatography (benzene–ethyl acetate; 98:2) to give tigogenin acetate (26) (91.6 mg, 92%), identical with an authentic sample. Two experiments with smaller amounts of iodine have been performed under the conditions shown in Table 2.

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