Tandem β-Fragmentation−Hydrogen Abstraction Reaction of Alkoxy Radicals in Steroidal Systems

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A number of tertiary or hemiacetalic steroidal alcohols, 2-hydroxy-3,4-dinor-2,3-secocholestan-5-one 2,5-hemiacetal (**1**), 2β,3β-dihydro-3'*H*-cyclopropa[2,3]-cholestan-5α-ol (**7**), 3β-phenyl-5α-hydroxycholestan-2-one (**10**), 5α-hydroxycholestan-3-one (**15**), 3β,5α-dihydroxycholestan-7-one 3-acetate (**21**), and 4,4-dimethyl-19-hydroxy-5α-cholestan-3-one 19,3-hemiacetal (**27**) have been prepared in order to test a new tandem β-fragmentation−hydrogen abstraction reaction. The alkoxy radicals generated by irradiation of these alcohols with visible light in the presence of (diacetoxyiodo)-benzene, iodine, and molecular oxygen undergo a β-fragmentation reaction followed by peroxidation of the C-radical formed. The peroxy radical reacts further with iodine to give an alkoxy radical and iodoxyl radical (IO•). The new alkoxy radical can produce intramolecular functionalization of suitably positioned carbons by hydrogen abstraction through a six-membered cyclic transition state to give tetrahydrofurans or can be intramolecularly trapped by carbonyl groups suitably disposed so as to generate a new alkoxy radical that can afford γ-lactones by β-fragmentation.

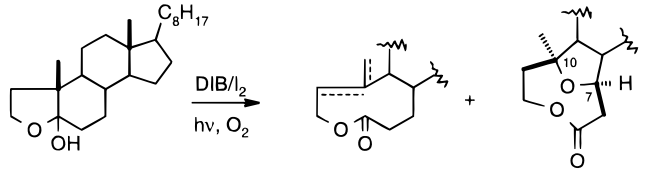
Radical tandem reactions as a methodology for linking two or more synthetic operations in a single step have received considerable attention in recent years for the preparation of complex molecules.[1]

In previous papers, we have reported the radical β-fragmentation of oxabicyclic hemiacetals, using hypervalent organoiodine reagents as a convenient synthesis of medium-sized and spiro-lactones by ring-expansion reaction.[2] During the past few years, we have also examined the use of these reagents in a related β-fragmentation of carbohydrate anomeric alkoxy radicals.[3]

In one of our earliest models, the steroidal hemiacetal **1**[2b] (Scheme 1), we observed that when the reaction was performed by irradiation with visible light in the presence of (diacetoxyiodo)benzene (DIB) and iodine under argon with rigorous exclusion of air only the mixture of unsaturated lactones **2a,b**[2b] was obtained in 85% yield. Nevertheless, in the presence of oxygen a new compound **3** was formed in moderate yield (Table 1, entries 1 and 2). It was evident from ^{1}H and ^{13}C NMR spectroscopy that a new oxygen bridge was formed between C_{10} and C_7.

Since the crystals of compound **3** were not suitable, its structure and stereochemistry were confirmed by single-crystal X-ray diffraction of the diester derivative **6**.[4]

Scheme 1



Compound **6** was prepared in 77% overall yield by the sequence shown in Scheme 2 involving lactone reduction with $LiAlH_4$ to the diol **4**, Jones reagent[5] oxidation, and methylation of the resulting diacid **5** with diazomethane.

A plausible mechanism for the formation of ether **3** is outlined in Scheme 3. The alkoxy radical I initially formed underwent β-fragmentation through C_5-C_{10} to provide a C_{10} radical II. Under argon, radical II was stabilized by elimination to give the mixture of olefins **2a,b**. Notwithstanding, under an oxygen atmosphere the radical II was stereoselectively peroxidated with inversion of configuration to afford peroxy radical III. The formation of peroxy radicals during these reactions has been proved by intramolecular trapping with suitably positioned functions, e.g., double bonds and carbonyl and carboxyl groups.[6] Homolysis of the hydroperoxide O−O bond led to alkoxy radical IV, which underwent hydrogen abstraction from C_7 to give the tetrahydrofuran derivative **3**.[7] This transformation of peroxy radicals into

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(4) The author has deposited the atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

(5) Bowers, A.; Halsall, T. G.; Jones, E. R. H.; Lemin, A. J. *J. Chem. Soc.* **1953**, 2548−2560.

(6) (a) Boto, A.; Betancor, C.; Prangé, T.; Suárez, E. *Tetrahedron Lett.* **1992**, *33*, 6687−6690. (b) Boto, A.; Betancor, C.; Hernández, R.; Rodríguez, M. S.; Suárez, E. *Tetrahedron Lett.* **1992**, *33*, 4865−4868. (c) Boto, A.; Betancor, C.; Prangé, T.; Suárez, E. *J. Org. Chem.* **1994**, *59*, 4393−4401. (d) Boto, A.; Betancor, C.; Hernández, R.; Rodríguez, M. S.; Suárez, E. *J. Org. Chem.* **1995**, *60*, 8209−8217.

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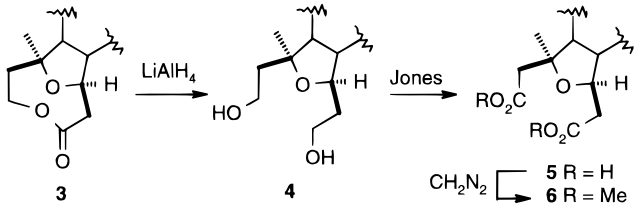
Table 1[a]

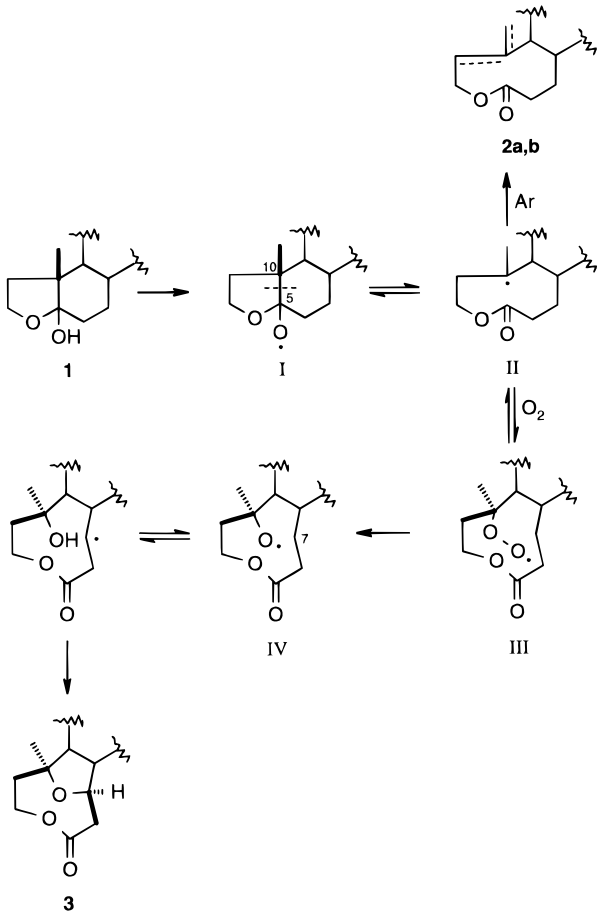
entry	substrate	reagent[b] (mmol)	I_2[b] (mmol)	P (atm)	*T* (°C)	time (h)	products (yield, %)
1	**1**	DIB (1.1)	1.0	air (1)	40	1	**2a,b** (38), **3** (29)
2	**1**	DIB (1.1)	1.0	O_2 (1)	40	1.3	**2a,b** (14), **3** (35)
3	**7**	DIB (3.7)	2.0	Ar (1)	40	1	**8** (71)
4	**7**	DIB (2.5)	1.5	O_2 (3)	40	1	**8** (21), **9** (30)
5	**7**	DIB (2.5)	1.5	O_2 (5)	40	1.75	**8** (18), **9** (39)
6	**7**	DIB (3.5)	1.4	O_2 (10)	rt	1.3	**8** (20), **9** (26)
7	**10**	DIB (2.0)	1.2	air (1)	40	2	**13** (10), **14** (16)
8	**10**	HgO (3.0)[c]	1.6	air (1)	40	1	**13** (17), **14** (20)
9	**10**	DIB (3.5)	1.5	O_2 (3.5)	40	1	**14** (49)
10	**15**	DIB (2.5)	2.0	air (1)	40	0.75	**17** (2), **18** (3)
11	**15**	HgO (3.1)[c]	1.4	air (1)	rt	1	**16** (28), **18** (23)
12	**15**	DIB (2.0)	1.0	O_2 (3)	40	0.5	**16** (10), **17** (13), **18** (10)
13	**15**	DIB (2.5)	1.5	O_2 (10)	rt	3	**16** (4), **17** (19), **18** (7)
14	**21**	DIB (1.5)	1.0	air (1)	40	5	**25**(10)
15	**21**	HgO (5.0)[c]	3.0	air (1)	45	3	**25** (9)
16	**21**	HgO (5.0)[c]	3.0	O_2 (3)	45	1.5	**25** (12)
17	**27**	DIB (1.5)	1.0	O_2 (1)	40−45	3	**28** (42), **29** (18)
18	**27**	DIB (1.5)	1.0	O_2 (5)	40−45	2	**28** (23), **29** (46)
19	**27**	DIB (1.5)	1.0	O_2 (10)	40−45	4	**28** (11), **29** (51)
20	**27**	$Hg(OAc)_2$ (1.5)	1.0	O_2 (10)	40−45	4	**28** (13), **29** (56)
21	**27**	LTA (3.0)	1.0	O_2 (10)	40−45	2	**28** (21), **29** (48)
22	**27**	HgO (3.0)	1.0	O_2 (10)	40−45	2	**28** (18), **29** (39)

[a] All reactions were irradiated with two 100 W tungsten-filament lamps in cyclohexane solution; those under pressure were performed in a borosilicate Griffin−Worden pressure vessel (Kontes-767100). [b] Per mmol of substrate. [c] Using CCl_4 as solvent. DIB = (diacetoxyiodo)benzene. LTA = lead tetraacetate.

Scheme 2



Scheme 3



alkoxy radicals deserves some comment. The homolytic cleavage of the weak O−O bond catalyzed by acids or low-valent transition metals is a very well-documented process and has synthetic and biological importance.[8] In our case, the cleavage may be catalyzed by iodine according to the following equation.

$$ROO^{\bullet} + I_2 \rightarrow ROI + OI^{\bullet}$$

Iodoxyl radical (OI•) has been detected in the vapor phase during the ozonolysis of the halogen[9] and postulated to be formed in solution by irradiation using a high-pressure mercury lamp of red mercury(II) oxide and iodine.[10] It is also worth noting here that the reaction occurs with absolute diastereoselectivity with the oxygen attack taking place with inversion of configuration at C_{10}. Presumably, the steroidal framework helps to direct the incoming oxygen on steric grounds.

With the dual purpose of examining the scope of the reaction and gaining insight into its mechanism, we have prepared several steroidal models (see Table 1). Alcohol **7** was synthesized by Simmons−Smith reaction on 5α-hydroxycholest-2-ene[11] also in order to investigate if the peroxy radical could be added to the 2,3-cyclopropane ring, but under the conditions shown in Table 1 (entries 3−6) only the cyclodecenone derivative **8** and the ether **9** were obtained. The photolysis was performed under different oxygen pressures, the best yield of tetrahydrofuran **9** being obtained at 5 atm (Table 1, entry 5) (Scheme 4). Increasing oxygen pressure from 5 to 10 atm does not enhance the yield (compare entries 5 to 6, Table 1).

(7) For a recent review on intramolecular free-radical abstraction see: Majetich, G.; Wheless, K. *Tetrahedron* **1995**, *51*, 7095−7129.

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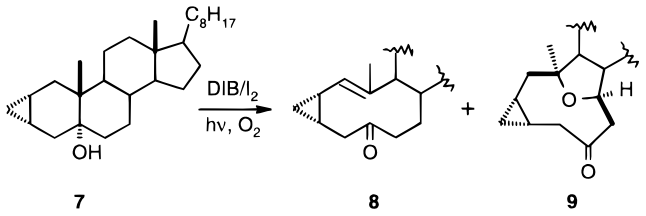
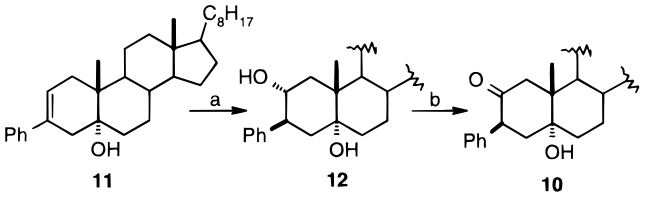
Scheme 4

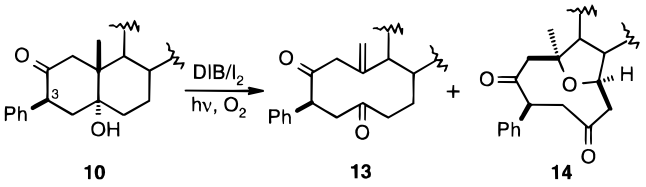


Scheme 5[a]

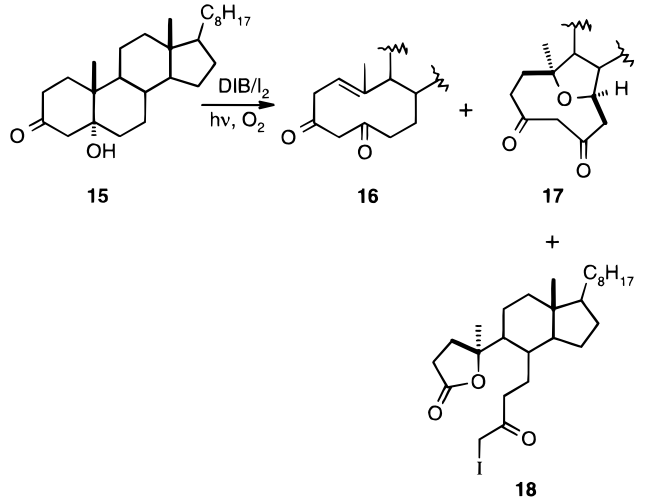


[a] Key: (a) BH_3·THF, 0 °C → rt, 10 h; NaOH, H_2O_2, rt, 1 h; (b) PCC, CH_2Cl_2, rt, 2 h.

Scheme 6



Scheme 7

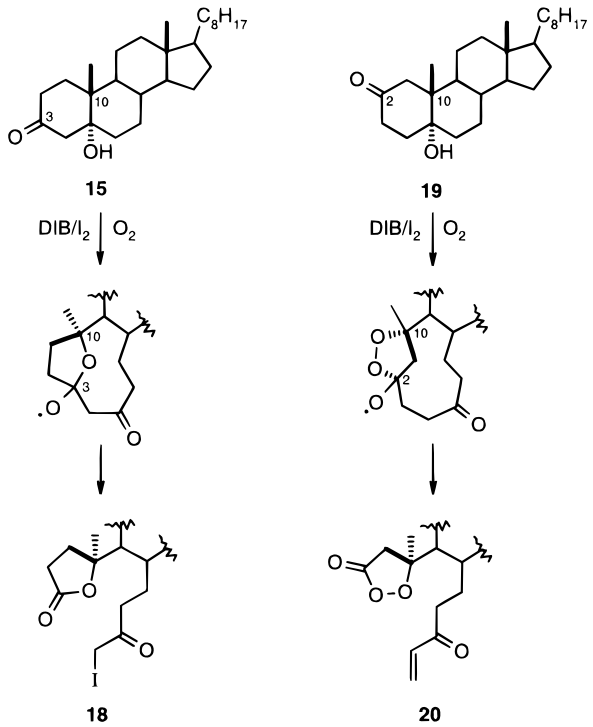


The synthesis of the steroidal model **10** was realized as shown in Scheme 5. The known homoallylic alcohol **11**[6c] by oxidative hydroboration afforded diol **12**, which on treatment with PCC led to **10** in good yield. Photolysis of **10** under air in the presence of DIB or HgO and iodine (entries 7 and 8) gave a mixture of two products **13** and **14** (Scheme 6). Irradiation at 3.5 atm of oxygen pressure gave the best result for tetrahydrofuran **14** formation (Table 1, entry 9). However, somewhat unexpectedly, we have not isolated any compound coming from an abstraction of the benzylic proton at C_3.

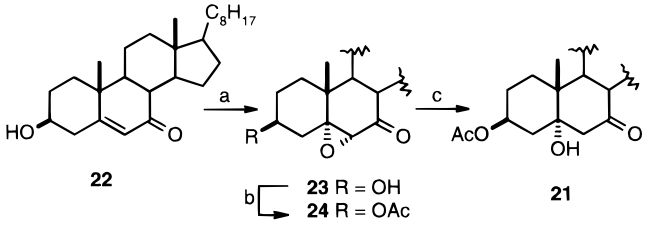
When we applied this methodology to steroidal hydroxy ketone **15**[6c] (Scheme 7) we obtained a γ-lactone **18** in low yield apart from the diketone **16** and the tetrahydrofuran **17** (Table 1, entries 10−13).[12] The formation of this

(12) For a preliminary communication see: Boto, A.; Hernández, R.; Suárez, E. *Tetrahedron Lett.* **1994**, *35*, 2597−2600.

Scheme 8



Scheme 9[a]



[a] Key: (a) H_2O_2, NaOH, MeOH, rt, 3 h; (b) Ac_2O, Py, rt, 15 h; (c) $(PhSe)_2$, $NaBH_4$, EtOH, 4 °C, 10 min.

γ-lactone **18** confirms the mechanism proposed for the tetrahydrofuran (Scheme 3) since the intervention of an alkoxy radical intermediate at C_{10} is necessarily involved. As shown in Scheme 8, the addition of this alkoxy radical to the carbonyl group at C_3 generates a new alkoxy radical that, in turn, undergoes a β-fragmentation to give γ-lactone **18**.

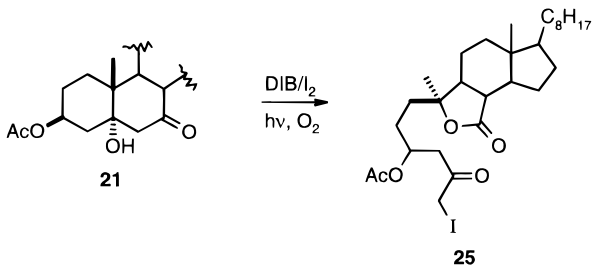
Previous observations from our laboratory[6d] in which 5-hydroxy-5α-cholestan-2-one (**19**) under these conditions underwent a C_{10} radical peroxidation and a subsequent addition of the peroxy radical to the C_2 carbonyl group followed by β-fragmentation (Scheme 8) to give a β-peroxy lactone **20** also provide good support for the proposed mechanism.

The β-hydroxy ketone **21** was synthesized, starting from **22** through epoxidation with 30% hydrogen peroxide and reduction[13] of the oxirane **24** with sodium phenylselenide[14] (Scheme 9), in order to trap the alkoxy radical with a carbonyl group at C_7 in the same place where the hydrogen abstraction takes place. As expected, a γ-lactone **25** is obtained during the photolysis of **21** although in low yield (Table 1, entries 14−16) (Scheme 10).

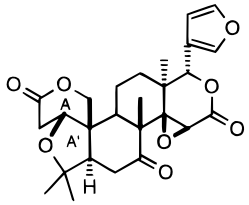
(13) Miyashita, M; Suzuki, T.; Yoshikoski, A. *Tetrahedron Lett.* **1987**, *28*, 4293−4296.

(14) (a) Sharpless, K. B.; Lauer, R. F. *J. Am. Chem. Soc.* **1973**, *95*, 2697−2699. (b) Haraguchi, K.; Tanaka, H.; Maeda, H.; Itoh, Y.; Saito, S.; Miyasaka, A. *J. Org. Chem.* **1991**, *56*, 5401−5408.

Scheme 10



This reaction may have interesting applications in synthetic organic chemistry. We have used it in a short and efficient synthesis of A and A′ rings of limonin (**26**) and related compounds.[15]



Limonin (**26**)

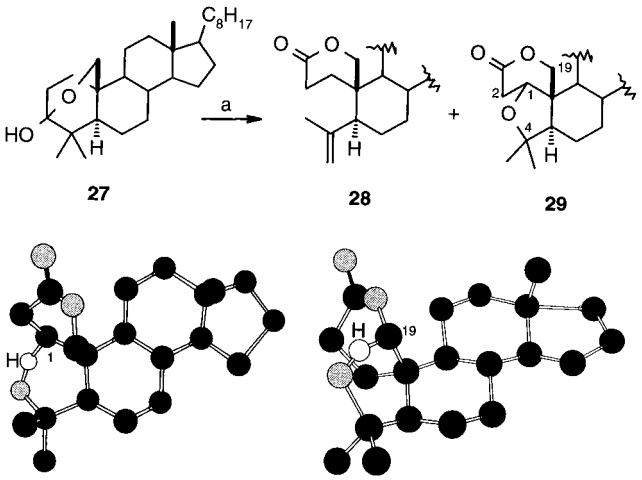
Limonin, the principal limonoid constituent of Citrus seeds, has been known for over 100 years.[16] However, it was not until 1960 that its structure was fully determined.[17] Although in the course of this structure elucidation much interesting chemistry has been developed, relatively little attention has been directed to its synthesis.[18]

The hemiacetal **27** was prepared according to a previously reported procedure[2b] (Scheme 11). Reaction of **27** with the system DIB/I_2 at different oxygen pressures (Table 1, entries 17−19) gave, apart from the expected spirolactone **28**,[2b] a new compound **29** with the same A and A′ ring system as limonin. As shown in Table 1, the yield of **29** increases with increasing oxygen pressure, reaching 51% at 10 atm (Table 1, entry 19). Various reagent systems were also studied ($Hg(OAc)_2/I_2$, LTA/I_2, and HgO/I_2), the best yield (56%) being obtained with $Hg(OAc)_2/I_2$ at 10 atm of oxygen pressure (Table 1, entry 20).

The structure of **29** was confirmed by spectroscopic data, the chemical shift and shape of the signals of the protons at C_1, C_2, and C_{19} being identical with those found in the downfield portion of the ^{1}H NMR spectra of limonin derivatives.[18b]

At first sight it is not clear why the alkoxy radical at C_4 abstracts exclusively a hydrogen at C_1 and not at C_{19},

Scheme 11. Transition States of H−C_1 and H−C_{19} Hydrogen Abstraction (Hydrogens and the Side Chain Are Omitted for Clarity)[a]



[a] Key: (a) see Table 1.

since a hydrogen abstraction at this latter position should be favored. Futhermore, the distances between the alkoxy radical and the abstractable hydrogens, measured in a minimized structure, are very similar (O···H−C_1 = 2.4 Å and O···H−C_{19} = 2.6 Å), and both are within the range where this reaction occurs.[19] Nevertheless, the energy of the six-membered transition state for the H−C_{19} intramolecular hydrogen abstraction calculated by using a MM2 forcefield model[20] was found to be 6.4 kcal/mol higher than the corresponding energy of the transition structure for the abstraction of the H−C_1, and this can explain the observed regioselectivity of the reaction (Scheme 11).

Although the reaction yield is moderate it compares favorably with that obtained in a multistep synthesis using a similar starting material.[18b]

Experimental Section

General Methods. Melting points were determined with a hot-stage apparatus and are uncorrected. Optical rotation measurements were recorded at room temperature in $CHCl_3$. IR spectra were recorded in $CHCl_3$ solutions. NMR spectra were determined at 200 or 400 MHz for ^{1}H and 50.3 MHz for $_{13}$C for $CDCl_3$ solutions in the presence of TMS as internal standard. Mass spectra were determined at 70 eV. Merck silica gel 60 PF_{254} and 60 (0.063-0.2 mm) were used for preparative thin-layer chromatography (TLC) and column chromatography, respectively. Circular layers of 1 mm of Merck silica gel 60 PF_{254} were used on a Chromatotron for centrifugally assisted chromatography. Commercial reagents and solvents were analytical grade or were purified by standard procedures prior to use. All reactions involving air- or moisture-sensitive materials were carried out under an argon atmosphere. Photolyses under oxygen pressure were performed in a borosolicate Griffin−Worden pressure vessel (Kontes K-767100). The spray reagent for TLC was vanillin (1 g) in H_2SO_4−EtOH (4:1; 200 mL). (Diacetoxyiodo)benzene (DIB) 98% was purchased from Aldrich.

General Procedure: Photolysis of 2-Hydroxy-3,4-dinor-2,3-secocholestan-5-one 2,5-Hemiacetal (1) under Oxygen. A solution of hemiacetal **1**[2b] (173 mg, 0.46 mmol) in cyclohexane (46 mL) containing (diacetoxyiodo)benzene (DIB)

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(164 mg, 0.51 mmol) and I_2 (117 mg, 0.46 mmol) was irradiated with two 100 W tungsten-filament lamps while air was bubbled through the mixture, at 40 °C for 1 h. The reaction mixture was then poured into a 10% aqueous sodium thiosulfate solution and extracted with dichloromethane. The organic layer was washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure. Column chromatography of the residue (benzene−EtOAc, 80:20) gave lactone **3** (52 mg, 0.13 mmol, 29%) and a mixture of two products that was rechromatographed (benzene−hexanes, 80:20), yielding lactone **2a**[2b] (35 mg, 0.093 mmol, 20%) and lactone **2b**[2b](31 mg, 0.083 mmol, 18%). Lactone **3**: mp 90−91 °C (from *n*-pentane); $[\alpha]_D$ +24° (c = 0.130); IR 1755, 1725 cm^{-1}; ^{1}H NMR 0.64 (3H, s), 0.82 (6H, d, J = 6.5 Hz), 0.88 (3H, d, J = 6.4 Hz), 1.23 (3H, s), 2.65, 3.01 (2H, ddd, J = 3.9, 3.7, 14.6 Hz), 3.88 (1H, m), 4.11 (1H, m), 4.64 (1H, t, J = 10.9 Hz); ^{13}C NMR 12.61 (q), 18.78 (q), 21.17 (t), 22.56 (q), 22.82 (q), 23.89 (t), 23.96 (t), 28.04 (q), 28.14 (d), 28.59 (t), 35.59 (d), 36.28 (t), 37.08 (t), 38.99 (t), 39.51 (t), 41.82 (t), 44.40 (s), 46.42 (d), 53.37 (d), 55.35 (d), 57.89 (d), 66.23 (t), 75.74 (d), 80.86 (s), 174.25 (s); MS m/z (rel intensity) 390 (M$^+$, 45), 362 (1), 347 (10), 333 (6), 318 (25), 302 (17), 277 (2), 275 (60), 247 (19), 205 (13); HRMS calcd for $C_{25}H_{42}O_3$ 390.3133, found 390.3124. Anal. Calcd for $C_{25}H_{42}O_3$: C, 76.86; H, 10.84. Found: C, 76.69; H, 10.91. Photolysis was also performed with DIB/I_2 under O_2 (1 atm) (Table 1, entry 2).

(1*R*,1′*R*,3*S*,3a*S*,5a*R*,6*R*,8a*S*,8b*S*)-[6-(1′,5′-Dimethylhexyl)-1-[(methoxycarbonyl)methyl]-3,5a-dimethyldecahydroindeno[4,5-*c*]furan-3-yl]acetic Acid Methyl Ester (6). A solution of lactone **3** (40 mg, 0.10 mmol) in dry THF (10 mL) was treated with $LiAlH_4$ (39 mg, 1.0 mmol) and stirred at rt for 45 min. The mixture was treated dropwise with saturated aqueous sodium sulfate. The precipitate was filtered off and washed thoroughly with diethyl ether, and the filtrate and the washing were combined, dried (Na_2SO_4), and evaporated under reduced pressure. Chromatotron chromatography of the residue (hexanes−EtOAc, 60:40) gave diol **4** (38 mg, 0.096 mmol, 96%), which was dissolved in acetone and treated with an excess of Jones reagent[5] at rt. The mixture was stirred for 1 h and then poured into water and extracted with dichloromethane. The organic layer was dried and concentrated as usual. To a solution of the crude diacid **5** in ether was added an excess of diazomethane in ether. The mixture was stirred for 15 min and the solvent evaporated under reduced pressure. The residue was purified by chromatotron chromatography (benzene−EtOAc, 90:10) to give ester **6** (35 mg, 0.077 mmol, 80%): mp 61−63 °C (from MeOH); $[\alpha]_D$ −11° (c = 0.20); IR 1725 cm^{-1}; ^{1}H NMR 0.67 (3H, s), 0.85 (6H, d, J = 6.2 Hz), 0.91 (3H, d, J = 6.4 Hz), 1.41 (3H, s), 2.27 (1H, d, J = 13.1 Hz), 2.39 (1H, d, J = 13.1 Hz), 2.47 (1H, dd, J = 14.9, 7.5 Hz), 2.54 (1H, dd, J = 14.9, 3.9 Hz), 3.94 (1H, ddd, J = 3.9, 7.6, 9.3 Hz); ^{13}C NMR 12.51 (q), 18.87 (q), 21.46 (t), 22.63 (q), 22.86 (q), 23.96 (t), 24.18 (t), 26.30 (q), 28.06 (d), 28.79 (t), 35.65 (d), 36.33 (t), 39.34 (t), 39.58 (t), 40.26 (t), 43.10 (t), 44.28 (s), 46.01 (d), 51.37 (q), 51.54 (q), 52.63 (d), 55.25 (d), 57.90 (d), 78.32 (d), 81.74 (s), 171.42 (s), 171.95 (s); MS m/z (rel intensity) 450 (M$^+$, 15), 435 (4), 432 (6), 418 (4), 403 (3), 400 (8), 390 (3), 387 (7), 377 (100), 361 (8), 337 (14), 319 (17), 303 (24); HRMS calcd for $C_{27}H_{46}O_5$ 450.3345, found 450.3336. Anal. Calcd for $C_{27}H_{46}O_5$: C, 71.95; H, 10.29. Found: C, 72.05; H, 10.41.

2*β*,3*β*-Dihydro-3′*H*-cyclopropa[2,3]cholestan-5α-ol (7). The Simmons−Smith reagent (70 mg) in dry ether (0.25 mL) was treated with a catalytic amount of I_2 and stirred at rt until the brown color disappeared. Then, diiodomethane (125 μL, 500 mg, 1.87 mmol) and 5α-hydroxychlolest-2-eno[11] (230 mg, 0.60 mmol) were added. The mixture was stirred under argon at reflux temperature for 5 h, cooled at rt, and filtered. The solid residue was washed with diethyl ether, and the combined organic layers were poured into aqueous ammonium chloride and washed successively with aqueous sodium bicarbonate and brine. After drying and evaporation in the usual way, followed by chromatotron chromatography (hexanes−EtOAc, 98:2), compound **7** (177.5 mg, 0.44 mmol, 74%) and a small amount of starting material (29.3 mg, 0.08 mmol, 13%) were obtained. Compound **7**: mp 99−101 °C (from MeOH); $[\alpha]_D$ +11.6° (c = 0.21); IR 3590 cm^{-1}; ^{1}H NMR 0.51 (2H, m), 0.64 (3H, s), 0.86 (6H, d, J = 7 Hz), 0.89 (3H, d, J = 7 Hz), 0.97 (3H, s); ^{13}C NMR 7.35 (d), 8.47 (d), 12.16 (q), 12.22 (t), 16.17 (q), 18.81 (q), 21.12 (t), 22.71 (q), 22.97 (q), 24.04 (t), 24.34 (t), 26.47 (t), 28.16 (d), 28.37 (t), 32.39 (t), 34.47 (t), 35.85 (d), 35.98 (d), 36.24 (t), 36.34 (t), 38.67 (s), 39.68 (t), 40.22 (t), 42.60 (s), 46.59 (d), 56.40 (d), 56.42 (d), 73.61 (s); MS m/z (rel intensity) 400 (M$^+$, 4), 385 (5) 382 (8), 367 (7), 332 (100), HRMS calcd for $C_{28}H_{48}O$, 400.3705, found 400.3711. Anal. Calcd for $C_{28}H_{48}O$: C, 83.92; H, 12.08. Found: C, 83.69; H, 12.25.

Photolysis of 2*β*,3*β*-Dihydro-3′*H*-cyclopropa[2,3]-cholestan-5α-ol (7). See full experimental details for entries 3−6 of Table 1 in the Supporting Information. Compound **8**: mp 122.5−124.5 °C (from MeOH−EtOAc); $[\alpha]_D$ −28.3° (c = 0.3); IR 1690 cm^{-1}; ^{1}H NMR 0.36 (1H, m), 0.69 (3H, s), 0.86 (6H, d, J = 6.7 Hz), 0.90 (3H, d, J = 8.0 Hz), 1.54 (3H, s), 4.92 (1H, d, J = 6.6 Hz); ^{13}C NMR 11.93 (q), 13.26 (d), 14.00 (q), 14.38 (t), 14.90 (d), 18.92 (q), 22.71 (q), 22.97 (q), 23.98 (t), 25.47 (t), 25.95 (t), 27.81 (t), 28.16 (d), 29.81 (t), 35.88 (d), 36.28 (t), 39.21 (t), 39.66 (t), 40.04 (d), 40.94 (t), 42.83 (s), 46.54 (t), 56.05 (d), 56.25 (d), 56.41 (d), 126.90 (d), 142.45 (s), 214.31 (s); MS m/z (rel intensity) 398 (M$^+$, 14), 383 (4), 380 (9); HRMS calcd for $C_{28}H_{46}O$ 398.3549, found 398.3577. Anal. Calcd for $C_{28}H_{46}O$: C, 84.35; H, 11.64. Found: C, 84.57; H, 11.47. Compound **9**: amorphous; $[\alpha]_D$ +2° (c = 0.14); IR 1690 cm^{-1}; ^{1}H NMR −0.13 (1H, m), 0.62 (3H, s), 0.88 (6H, d, J = 6.6 Hz), 0.94 (3H, d, J = 6.4 Hz), 1.27 (3H, s), 2.86 (1H, t, J = 11 Hz), 3.05 (1H, dd, J = 4.3, 13.8 Hz), 3.82 (1H, m); ^{13}C NMR 12.79 (q), 13.60 (t), 14.63 (d), 17.10 (d), 18.96 (q), 21.20 (t), 22.71 (q), 22.96 (q), 24.00 (t), 24.30 (t), 28.17 (d), 28.76 (t), 29.95 (q), 35.74 (d), 36.41 (t), 39.66 (2 × t), 41.89 (t), 42.09 (t), 44.27 (s), 45.75 (d), 49.41 (t), 53.66 (d), 55.31 (d), 56.59 (d), 78.71 (d), 83.62 (s), 213.63 (s); MS m/z (rel intensity) 414 (M$^+$, 27), 399 (3), 396 (3); HRMS calcd for $C_{28}H_{46}O_2$ 414.3498, found 414.3505. Anal. Calcd for $C_{28}H_{46}O_2$: C, 81.09; H, 11.19. Found: C, 81.21; H, 11.05.

3*β*-Phenylcholestane-2α,5α-diol (12). 3-Phenylcholest-2-en-5α-ol (**11**)[6c] (150 mg, 0.32 mmol) in dry THF (10 mL) was treated with a 1 M solution of borane in THF (2 mL, 2 mmol), which was added dropwise at 0 °C under argon. The solution was allowed to reach rt and stirred for another 10 h and then was cooled in ice, and water was slowly added until evolution of hydrogen ceased. Afterwards, a 3 M aqueous solution of NaOH (3 mL) was added in one portion, and 30% hydrogen peroxide (3 mL) was dripped under vigorous stirring. The ice bath was removed, and the mixture was stirred for 1 h at rt and then poured into 5% aqueous HCl and extracted with dichloromethane. The organic layer was washed with water and brine, dried, and evaporated as previously described. Chromatotron chromatography (hexanes−EtOAc, 80:20) yielded 3*β*-phenylcholestane-3α,5α-diol[6c] (30 mg, 0.063 mmol, 20%) and 3*β*-phenylcholestane-2α,5α-diol **(12)** (95 mg, 0.2 mmol, 61%). Diol **12**: mp 169−171 and 177.8−179.5 °C (from EtOAc); $[\alpha]_D$ +2.1° (c = 0.33); IR 3600, 3400 cm^{-1}; ^{1}H NMR 0.68 (3H, s), 0.87 (6H, d, J = 6.6 Hz), 0.92 (3H, J = 6.4 Hz), 1.12 (3H, s), 3.05 (1H, m), 4.03 (1H, m), 7.24−7.38 (5H, m); ^{13}C NMR 12.09 (q), 17.32 (q), 18.59 (q), 21.17 (t), 22.49 (q), 22.75 (q), 23.81 (t), 24.03 (t), 26.00 (t), 27.94 (d), 28.19 (t), 33.36 (t), 33.98 (d), 35.75 (d), 36.10 (t), 39.43 (t), 39.82 (t), 39.90 (t), 40.71 (s), 42.32 (t), 42.65 (s), 45.96 (d), 47.60 (d), 56.02 (d), 56.16 (d), 71.25 (d), 73.25 (s), 126.77 (d), 128.00 (d), 128.69 (d), 142.97 (s); MS m/z (rel intensity) 480 (M$^+$, 6), 462 (100), 447 (29), 444 (66), 429 (9); HRMS calcd for $C_{33}H_{52}O_2$ 480.396 73, found 480.395 10. Anal. Calcd for $C_{33}H_{52}O_2$: C, 82.43; H, 10.91. Found: C, 82.39; H, 10.69.

3*β*-Phenyl-5α-hydroxycholestan-2-one (10). Diol **12** (85 mg, 0.18 mmol) in dichloromethane (20 mL) was treated with pyridinium chlorochromate (54 mg, 0.25 mmol) for 2 h. The mixture was then evaporated under vacuum and purified by column chromatography (hexanes−EtOAc, 90:10), yielding compound **10** (74 mg, 0.15 mmol, 87%): amorphous; $[\alpha]_D$ −5.8° (c = 0.17); IR 3600, 1700 cm^{-1}; ^{1}H NMR 0.68 (3H, s), 0.87 (6H, d, J = 6.6 Hz), 0.92 (3H, d, J = 6.4 Hz), 1.03 (3H, s), 2.29 (1H, d, J = 13.5 Hz), 2.76 (1H, d, J = 13.4 Hz), 4.06 (1H, dd, J = 12.7, 6.9 Hz), 7.12−7.38 (5H, m); ^{13}C NMR 11.99 (q), 17.14 (q), 18.59 (q), 21.09 (t), 22.49 (q), 22.75 (q), 23.80 (t), 24.08 (t), 26.18 (t), 27.94 (d), 28.15 (t), 33.29 (t), 34.22 (d), 35.72 (d), 36.09 (t), 39.43 (t), 39.69 (t), 42.52 (s), 44.18 (s), 44.70 (t), 45.47 (d),

48.47 (t), 52.65 (d), 55.98 (d), 56.16 (d), 73.02 (s), 126.80 (d), 128.31 (d), 128.90 (d), 138.58 (s), 210.67 (s); MS *m/z* (rel intensity) 478 (M^+, 6), 460 (1), 418 (37); HRMS calcd for $C_{33}H_{50}O_2$ 478.381 08, found 478.380 99. Anal. Calcd for $C_{33}H_{50}O_2$: C, 82.78; H, 10.53. Found: C, 82.51; H, 10.73.

Photolysis of 3β-Phenyl-5α-hydroxycholestan-2-one (10). See full experimental details for entries 7−9 of Table 1 in the Supporting Information. Compound **13**: mp 88.2−90.2 °C (from MeOH−water); $[\alpha]_D$ +131° (c = 0.13); IR 1700 cm^{-1}; ^1H NMR 0.72 (3H, s), 0.86 (6H, d, J = 6.6 Hz), 0.89 (3H, d, J = 6.2 Hz), 2.27 (1H, m), 2.46 (1H, dd, J = 3.3, 15.4 Hz), 2.76 (1H, m), 3.11, (1H, d, J = 12.8 Hz), 3.20 (1H, d, J = 12.8 Hz), 3.53 (1H, dd, J = 15.4, 12.7 Hz), 4.73 (1H, dd, J = 12.7, 3.3 Hz), 5.13 (2H, s), 7.27−7.36 (5H, m); ^{13}C NMR 11.92 (q), 18.67 (q), 22.55 (q), 22.80 (q), 23.77 (t), 24.83 (t), 26.77 (t), 27.92 (t), 28.01 (d), 29.69 (t), 35.70 (d), 36.11 (t), 37.60 (d), 39.50 (t), 39.61 (t), 42.85 (s), 49.26 (t), 56.04 (d), 127.71 (d), 128.15 (d), 129.00 (d), 137.54 (s), 147.02 (s), 207.59 (s), 210.03 (s), due to the slow conformational equilibrium of the medium-sized ring, only 25 well-defined signals were observed; MS *m/z* (rel intensity) 476 (M^+, 5), 458 (1); HRMS calcd for $C_{33}H_{48}O_2$ 476.365 43, found 476.366 11. Anal. Calcd for $C_{33}H_{48}O_2$: C, 83.13; H, 10.16. Found: C, 83.05; H, 10.42. Compound **14**: amorphous; $[\alpha]_D$ +142° (c = 0.11); IR 1705 cm^{-1}; ^1H NMR 0.71 (3H, s), 0.87 (6H, d, J = 6.4 Hz), 0.92 (3H, d, J = 6.5 Hz), 1.39 (3H, s), 2.39 (1H, d, J = 11.9 Hz), 2.50 (1H, dd, J = 3.3, 15 Hz), 2.52 (1H, dd, J = 3.6, 11.4 Hz), 2.68 (1H, d, J = 11.9 Hz), 3.24 (1H, dd, J = 15, 12.7 Hz), 3.25 (1H, m), 3.94 (1H, m), 5.15 (1H, dd, J = 3.3, 12.7 Hz), 7.3−7.4 (5H, m); ^{13}C NMR 12.46 (q), 18.76 (q), 21.88 (t), 22.54 (q), 22.79 (q), 23.76 (t), 23.84 (t), 28.00 (d), 28.64 (t), 29.79 (q), 35.58 (d), 36.23 (t), 39.36 (t), 39.49 (t), 44.36 (s), 44.46 (d), 47.68 (t), 49.15 (t), 49.89 (t), 53.82 (d), 54.16 (d), 55.25 (d), 58.11 (d), 78.40 (d), 83.22 (s), 127.61 (d), 128.39 (d), 128.94 (d), 137.26 (s), 208.66 (s), 211.26 (s); MS *m/z* (rel intensity) 492 (M^+, 10), 474 (8), 450 (100); HRMS calcd for $C_{33}H_{48}O_3$ 492.360 35, found 492.360 43. Anal. Calcd for $C_{33}H_{48}O_3$: C, 80.43; H, 9.83. Found: C, 80.53; H, 9.97.

Photolysis of 5α-Hydroxycholestan-3-one (15). See full experimental details for entries 10−13 of Table 1 in the Supporting Information. Compound **16**: mp 130.6−132.5 °C (from *n*-hexane); $[\alpha]_D$ +327.7° (c = 0.36); IR 1720 cm^{-1}; ^1H NMR 0.71 (3H, s), 0.86 (6H, d, J = 7.4 Hz), 0.90 (3H, d, J = 7.0 Hz), 1.73 (3H, s), 2.68 (1H, dd, J = 14.8, 6 Hz), 2.84 (2H, d, J = 16 Hz), 3.49 (1H, dd, J = 11, 14.8 Hz), 4.32 (2H, d, J = 16 Hz), 5.23 (1H, m); ^{13}C NMR 11.87 (q), 18.60 (q), 18.93 (q), 22.53 (q), 22.75 (q), 23.63 (t), 23.97 (t), 25.65 (t), 26.90 (t), 27.86 (t), 27.97 (d), 35.61 (d), 36.06 (t), 36.61 (d), 39.18 (t), 39.47 (t), 40.37 (t), 41.46 (t), 42.12 (d), 42.82 (s), 50.20 (d), 52.08 (t), 55.79 (d), 118.63 (d), 144.62 (s), 203.77 (s), 208.94 (s); MS *m/z* (rel intensity) 400 (M^+, 36), 385 (4), 382 (7); HRMS calcd for $C_{27}H_{44}O_2$ 400.3341, found 400.333 64. Anal. Calcd for $C_{27}H_{44}O_2$: C, 80.94; H, 11.07. Found: C, 80.71; H, 10.85. Compound **17**: mp 64−66 °C (from MeOH); $[\alpha]_D$ +90° (c = 0.07); IR 1713, 1686 cm^{-1}; ^1H NMR 0.72 (3H, s), 0.87 (6H, d, J = 6.6 Hz), 0.93 (3H, d, J = 6.4 Hz), 1.26 (3H, s), 2.32 (1H, dd, J = 12.2, 2.8 Hz), 3.22 (1H, dd, J = 12.2, 5.4 Hz), 3.54 (2H, s), 3.87 (1H, m); ^{13}C NMR 12.55 (q), 18.71 (q), 21.18 (t), 22.54 (q), 22.80 (q), 23.82 (t), 23.82 (t), 24.93 (q), 28.00 (d), 28.64 (t), 33.58 (t), 35.55 (d), 36.20 (t), 39.15 (t), 39.46 (t), 40.50 (t), 43.83 (d), 44.27 (s), 45.39 (t), 52.89 (d), 55.22 (d), 56.78 (d), 60.02 (t), 78.18 (d), 82.25 (s), two carbons were not observed; MS *m/z* (rel intensity) 416 (M^+, 22), 398 (2), 401 (2); HRMS calcd for $C_{27}H_{44}O_3$ 416.329 04, found 416.329 38. Anal. Calcd for $C_{27}H_{44}O_3$: C, 77.82; H, 10.65. Found: C, 77.73; H, 10.51. Compound **18**: amorphous; $[\alpha]_D$ −39.1° (c = 0.27); IR 1765, 1710 cm^{-1}; ^1H NMR 0.7 (3H, s), 0.87 (6H, d, J = 6.5 Hz), 0.90 (3H, d, J = 6.2 Hz), 1.30 (3H, s), 3.87 (1H, d, J = 10.3 Hz), 4.13 (1H, d, J = 10.3 Hz); ^{13}C NMR 7.57 (t) 11.92 (q), 18.54 (q), 19.03 (q), 22.51 (q), 22.77 (q), 23.72 (t), 23.85 (t), 23.98 (t), 25.23 (t), 27.78 (t), 27.96 (d), 28.04 (t), 33.32 (t), 35.23 (t), 35.68 (d), 35.76 (d), 35.95 (t), 39.41 (t), 39.46 (t), 42.49 (s), 48.86 (d), 51.90 (d), 56.22 (d), 89.84 (s), 176.48 (s), 204.56 (s); MS *m/z* (rel intensity) 544 (M^+, 1), 417 (20), 403 (10), 399 (33), 385 (12), 99 (100), 43 (57); HRMS calcd for $C_{27}H_{45}IO_3$ 544.241 35, found 544.241 68. Anal. Calcd for $C_{27}H_{45}IO_3$: C, 59.53; H, 8.33. Found: C, 59.49; H, 8.41.

3β-Hydroxy-5α,6α-epoxycholestan-7-one (23). To a solution of 3β-hydroxycholest-5-en-7-one[21] (**22**) (600 mg, 1.5 mmol) in MeOH (57 mL) containing 8 N NaOH aqueous solution (0.98 mL) was added 30% hydrogen peroxide (3 mL) portionwise 1 mL every hour. The mixture was stirred at rt for 3 h, poured into 10% HCl, and extracted with CH_2Cl_2. The organic layer was washed with water, dried (Na_2SO_4), and evaporated under vacuum. Column chromatography of the residue (benzene−EtOAc, 4:1) afforded starting material (330 mg) and epoxide **23** (132 mg, 0.32 mmol, 21%): mp 165−166.5 °C (from acetone−*n*-hexane); $[\alpha]_D$ +98° (c = 0.338); IR 3609, 1694 cm^{-1}; ^1H NMR 0.65 (3H, s), 0.85 (6H, d, J = 6.8 Hz), 0.89 (3H, d, J = 7.0 Hz), 1.01 (3H, s), 3.04 (1H, s), 3.89 (1H, m); ^{13}C NMR 12.01 (q), 15.48 (q), 18.65 (q), 21.10 (t), 22.49 (q), 22.75 (t), 23.77 (t), 24.81 (t), 27.92 (d), 28.24 (t), 30.77 (t), 32.76 (t), 34.98 (t), 35.81 (d), 36.01 (t), 38.68 (t), 39.33 (t), 39.59 (t), 43.25 (d), 43.93 (s), 46.73 (d), 51.87 (d), 55.21 (d), 62.98 (d), 68.12 (s), 68.59 (d), 207.84 (s); MS *m/z* (rel intensity) 416 (M^+, 13), 398 (16), 387 (26), 373 (53), 355 (9), 341 (16); HRMS calcd for $C_{27}H_{44}O_3$ 416.329 05, found 416.327 25. Anal. Calcd for $C_{27}H_{44}O_3$: C, 77.82; H, 10.65. Found: C, 78.01; H, 10.61.

3β-Hydroxy-5α,6α-epoxycholestan-7-one Acetate (24). A solution of **23** (122 mg, 0.29 mmol) in dry pyridine (2 mL) containing acetic anhydride (1 mL) was stirred at rt for 15 h. Workup as usual gave after chromatotron chromatography (benzene−EtOAc, 97:3) the acetate **24** (116 mg, 0.25 mmol, 86%): mp 129.5−130.5 °C (from *n*-hexane); $[\alpha]_D$ +79° (c = 0.204); IR 1732, 1694 cm^{-1}; ^1H NMR 0.66 (3H, s), 0.85 (6H, d, J = 6.6 Hz), 0.89 (3H, d, J = 6.9 Hz), 1.03 (3H, s), 2.02 (3H, s), 3.02 (1H, s), 4.91 (1H, m); ^{13}C NMR 12.02 (q), 15.38 (q), 18.68 (q), 21.07 (t), 21.16 (q), 22.52 (q), 22.77 (q), 23.79 (t), 24.84 (t), 27.05 (t), 27.92 (d), 28.26 (t), 32.51 (t), 35.04 (t), 35.12 (s), 35.83 (d), 36.04 (t), 39.40 (t), 39.58 (t), 43.18 (d), 43.93 (s), 46.69 (d), 51.85 (d), 55.22 (d), 62.80 (d), 67.54 (s), 70.79 (d), 170.00 (s), 207.28 (s); MS *m/z* (rel intensity) 458 (M^+, <1), 398 (4), 371 (23); HRMS calcd for $C_{29}H_{46}O_4$ 458.339 61, found 458.340 54. Anal. Calcd for $C_{29}H_{46}O_4$: C, 75.93; H, 10.11. Found: C, 76.02; H, 10.23.

3β,5α-Dihydroxycholestan-7-one 3-Acetate (21). To a solution of diphenyl diselenide (49 mg, 0.16 mmol) in ethanol (0.8 mL) was added $NaBH_4$ in small portions until disappearance of the yellow color was observed (15 mg, 0.39 mmol), and then acetic acid (3.2 μL) was added. This solution was added dropwise under argon to a solution of epoxy acetate **24** (45.8 mg, 0.1 mmol) in ethanol (2.1 mL), previously cooled to 4 °C with a water-ice bath. Once the addition was over, stirring continued for 10 min. The mixture was then poured into brine and extracted with CH_2Cl_2 and the residue purified by chromatotron chromatography (hexanes−EtOAc, 85:15) to give the acetate of enone **22** (5.2 mg, 0.012 mmol, 12%) and alcohol **21** (35 mg, 0.076 mmol, 76%): mp 220−222 °C (from acetone−*n*-hexane); $[\alpha]_D$ +41° (c = 0.186); IR 3594, 1716 cm^{-1}; ^1H NMR 0.65 (3H, s), 0.86 (6H, d, J = 6.4 Hz), 0.91 (3H, d, J = 6.4 Hz), 1.25 (3H, s), 2.02 (3H, s), 2.04 (1H, d, J = 13.1 Hz), 2.78 (6H, d, J 13.1 Hz) 5.11 (1H, m); ^{13}C NMR 12.06 (q), 16.17 (q), 18.73 (q), 21.34 (q), 21.69 (t), 22.50 (q), 22.74 (q), 23.79 (t), 24.98 (t), 26.53 (t), 27.95 (d), 28.45 (t), 30.20 (t), 35.63 (d), 36.11 (t), 38.83 (t), 39.35 (s), 39.41 (t), 39.65 (t), 42.80 (s), 47.02 (d), 48.75 (d), 50.16 (d), 52.67 (t), 54.93 (d), 70.49 (d), 79.11 (s), 170.84 (s), 210.34 (s); MS *m/z* (rel intensity) 460 (M^+, 1), 442 (<1), 400 (4), 382 (7); HRMS calcd for $C_{29}H_{48}O_4$ 460.355 26, found 460.354 45. Anal. Calcd for $C_{29}H_{48}O_4$: C, 75.59; H, 10.51. Found: C, 75.68; H, 10.69.

Photolysis of 3β,5α-Dihydroxycholestan-7-one 3-Acetate (21). See full experimental details for entries 14−16 of Table 1 in the Supporting Information. Lactone **25**: amorphous; IR 1762, 1736 cm^{-1}; ^1H NMR 0.68 (3H, s), 0.87 (6H, d, J = 6.6 Hz), 0.93 (3H, d, J = 6.4 Hz), 1.39 (3H, s), 2.05 (3H, s), 2.99 (1H, s), 3.81 (1H, d, J = 10 Hz), 3.84 (1H, d, J = 10 Hz), 5.23 (1H, m); ^{13}C NMR 6.09 (t), 12.19 (q), 18.77 (q), 21.04 (q), 21.48 (t), 22.52 (q), 22.77 (q), 22.92 (t), 23.83 (t), 24.36 (q), 27.97 (d), 28.16 (t), 28.56 (t), 29.22 (t), 35.58 (d), 36.14 (t), 38.83

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(t), 39.41 (t), 42.37 (d), 43.47 (t), 44.64 (s), 50.44 (d), 54.89 (d), 54.96 (d), 70.12 (d), 86.41(s), 170.47 (s), 176.77 (s), 199.76 (s); MS *m/z* (rel intensity) 542 (M^+ − AcOH, 3), 539 (4), 369 (40), 319 (60), 254 (78); HRMS calcd for $C_{27}H_{43}IO_3$ 542.225 70, found 542.227 22. Anal. Calcd for $C_{29}H_{47}IO_5$: C, 57.78; H, 7.87. Found: C, 57.83; H, 7.98.

Photolysis of 4,4-Dimethyl-19-hydroxy-5α-cholestan-3-one 19,3-Hemiacetal (27). See full experimental details for entries 17−22 of Table 1 in the Supporting Information. Lactone **29**: mp 119−120 °C (from *n*-pentane); $[\alpha]_D$ −19° (*c* = 0.20); IR 1740 cm^{-1}; ^1H NMR 0.65 (3H, s), 0.86 (6H, d, *J* = 6.5 Hz), 0.89 (3H, d, *J* = 6.2 Hz), 1.12 (3H, s), 1.25 (3H, s), 2.65 (1H, dd, *J* = 2.7, 17.1 Hz), 2.89 (1H, dd, *J* = 3.1, 17.1 Hz), 4.03 (1H, t, *J* = 2.9 Hz), 4.32 (1H, d, *J* = 12.8 Hz), 4.54 (1H, d, *J* = 12.8 Hz); ^{13}C NMR 12.22 (q), 18.82 (q), 21.18 (t), 22.67 (q), 22.79 (q), 22.94 (q), 23.74 (t), 23.94 (t), 24.67 (t), 28.04 (t), 28.13 (d), 30.90 (d), 31.92 (t), 35.50 (t), 35.57 (d), 35.80 (q), 36.24 (t), 39.36 (t), 39.60 (t), 42.73 (s), 45.26 (s), 52.32 (d), 56.12 (d), 56.27 (d), 60.61 (d), 66.24 (t), 78.00 (d), 80.82 (s), 170.78 (s); MS *m/z* (rel intensity) 444 (M^+, 4), 429 (100), 411 (7), 386 (5), 357 (4), 289 (28); HRMS calcd for $C_{29}H_{48}O_3$ 444.3693, found 444.3647. Anal. Calcd for $C_{29}H_{48}O_3$: C, 78.31; H, 10.89. Found: C, 78.52; H, 11.05.

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Supporting Information Available: Full description of the experimental procedures for entries 3−22 of Table 1 (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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