155. Synthesis, Structure, and Reactivity of Secosteroids Containing a Medium-Size Ring

Part 35[1])

Photooxidations of Some (*Z*)- and (*E*)-1(10)-Unsaturated 5,10-Secosteroids in Acetone Solution

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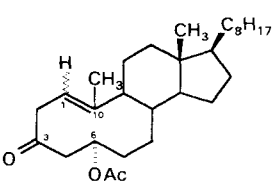
UV Irradiation of (*Z*)- and (*E*)-1(10)-unsaturated 5,10-secosteroids **1**–**4** in acetone solution effected, besides (*Z*/*E*)-isomerization, *i*) a stereospecific epoxidation (only in the presence of O_2), which, depending on the configuration ((*Z*) or (*E*)) in the starting steroid, gave *cis*-epoxides **5** and **8** (from the (*Z*)-compounds **1** and **3**) or *trans*-epoxides **6**, **9**, and **10** (from the (*E*)-compounds **2** and **4**), and *ii*) oxidative acetone addition to the olefinic double bond producing 1-acetonyl derivatives **7** and **11a**, **b**.

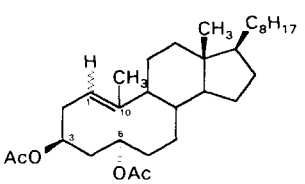
Introduction. – In a preliminary communication [2], we briefly described a novel photochemical reaction of the β,γ-enone grouping incorporated in the ten-membered ring of the (*Z*)- and (*E*)-3-oxo-5,10-secocholest-1(10)-en-5α-yl acetates (**1** and **2**, resp.), induced by UV light in acetone solution. Now we wish to report more extensively on the results obtained with these substrates and, in addition, with the structurally related 1(10)-unsaturated secosteroids (*Z*)- and (*E*)-5,10-secocholest-1(10)-ene-3β,5α-diyl diacetates (**3** and **4**, resp.), when subjected to UV light under experimental conditions similar to those applied to the enones **1** and **2**.

The syntheses of the (*Z*)- and (*E*)-acetates **1** and **2** [1] and of the (*Z*)- and (*E*)-diacetates **3** and **4** [3] (starting from the (*Z*)- and (*E*)-5-oxo-5,10-secocholest-1(10)-en-3β-yl acetates [4]) were previously described.

Results and Discussion. – UV Irradiation of compounds **1**–**4** was carried out in dioxane, i-PrOH, or acetone solution (*ca.* $2 \cdot 10^{-3}$ M) with a high-pressure mercury lamp



1 (*Z*)-isomer
2 (*E*)-isomer



3 (*Z*)-isomer
4 (*E*)-isomer

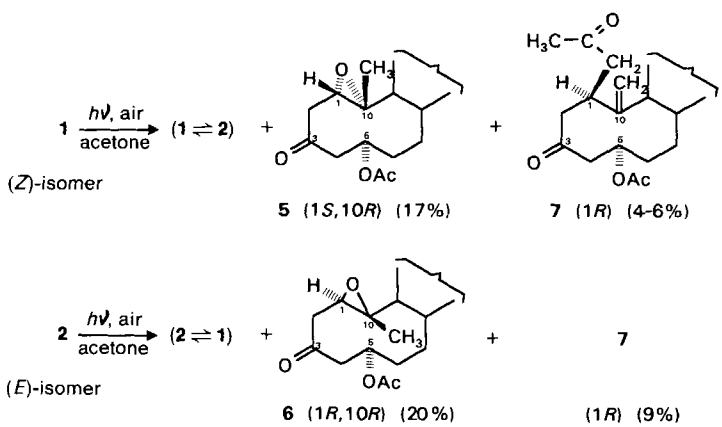
[1]) Part 34: [1].

(*TQ 150 Z2*) contained in a H_2O-cooled jacket of *Pyrex*, at room temperature for 4 h, with stirring. The reaction mixtures were separated by column chromatography on silica gel.

When **1** or **2** was irradiated in dioxane or i-PrOH solution in the presence of air, the only observable photoprocess was (*Z*/*E*)- (or (*E*/*Z*)-) isomerization of the olefinic 1(10)-double bond. With both substrates, after 4 h irradiation, a photostationary mixture of stereoisomers was obtained (the (*E*/*Z*)-ratio being *ca.* 1:1.1 and 1:1.6, resp.).

However, when similar irradiation of **1** and **2** was performed in acetone solution (from which air, as above, had not been expelled), besides (*Z*/*E*)-isomerization, two additional photochemical transformations involving participation of the solvent molecule took place as well (*Scheme 1*, *Table 1*), namely *i*) epoxidation of the olefinic double bond, which, depending on configuration, gave predominantly *cis*-epoxide **5** ((1*S*,10*R*); from (*Z*)-isomer **1**)[2]) and *trans*-epoxide **6** ((1*R*,10*R*); from (*E*)-isomer **2**), respectively, in *ca.* 20% yield, and *ii*) oxidative addition of the solvent molecule to the (*E*)-double bond, affording the (1*R*)-acetonyl derivative **7** as a single stereoisomer in less than 10% yield[3]).

Scheme 1



Similar results were obtained with **1** and **2** when O_2 was bubbled through the acetone solution during irradiation, while experiments carried out under N_2 did not give epoxidation products. However, in the latter case (*E*)-isomer **2** afforded the acetonyl derivative **7** in considerably higher yield (*ca.* 30–34%; *Table 1*), probably because under N_2, competing photoprocesses in which molecular O_2 is involved to not interfere with oxidative acetone addition to the (*E*)-double bond.

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[2]) In our preliminary communication [2], due to insufficient characterization of the epoxide fractions, it was erroneously concluded that photoepoxidation of the olefinic double bond in **1** and **2**, irrespective of the geometry of the starting enone, gave only *trans*-stereoisomer **6**.

[3]) Oxidative acetone addition to the (*Z*)-double bond would produce the (1*S*)-acetonyl derivative, which, however, was not detected. This suggests that the (1*R*)-acetonyl product **7**, obtained upon irradiation of the (*Z*)-isomer **1**, arises from the reaction of the (*E*)-isomer **2**, formed by (*Z*/*E*)-photoisomerization of the starting compound **1** (see *Table 1*).

Table 1. *Irradiation of* **1** *and* **2** *in Acetone Solution* (*ca.* $2 \cdot 10^{-3}$ M) *with a* TQ-150-Z2 *Lamp for 4 h*

Substrate	Conditions	Yields [%][a])				
		1	**2**	**5**	**6**	**7**
(*Z*)-Isomer **1**	*hv*, air	34	8	17	traces[b])	4–6
	hv, O_2	41	10	24	traces[b])	2
	hv, N_2	43	8	–	–	7
(*E*)-Isomer **2**	*hv*, air	32	8	traces[b])	20	9
	hv, O_2	31	7	traces[b])	14	10
	hv, N_2	48	11	–	–	30–34

[a]) All yields (average of at least 3 experiments) refer to crude products, separated by column chromatography on silica gel (yields after recrystallization were lower by 10–20%).

[b]) The presence of this stereoisomer in the crude epoxide fraction eluted from the SiO_2 column was detected by ^{1}H-NMR.

The structures of the epoxides **5** and **6** ($C_{29}H_{48}O_4$) were deduced from their spectral characteristics (IR, ^{1}H-NMR, and ^{13}C-NMR; see *Exper. Part*) and confirmed by synthesis; *i.e.*, 3-chloroperbenzoic acid oxidation of **1** and **2** gave the epoxy derivatives **5** and **6**, respectively, identical to those obtained in the photochemical reactions.

The photoproduct **7** ($C_{32}H_{52}O_4$) was identified on the basis of its MS (M^+ at m/z 500) IR, ^{1}H-NMR, and ^{13}C-NMR spectra (see *Exper. Part*). Moreover, the (1*R*)-configuration of **7** was unequivocally established by X-ray analysis (*Fig.*)[4]).

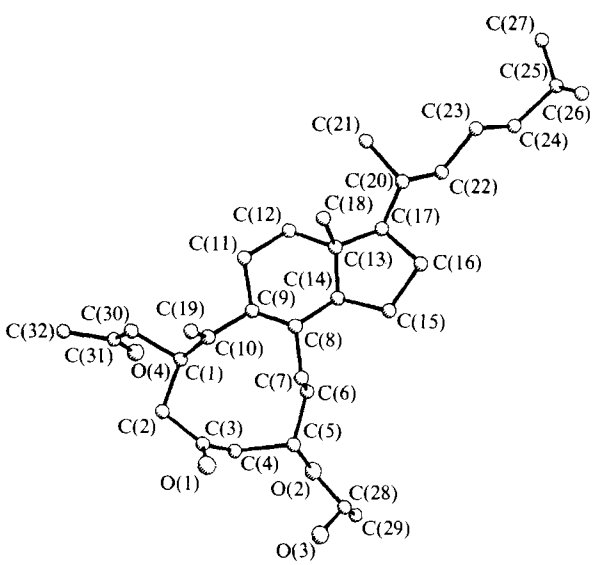

Figure. *Molecular structure of the (1R)-acetonyl product* **7**

[4]) We are grateful to Drs. *B. Tinant* and *J. P. Declercq*, who confirmed the structure and determined the (1*R*)-configuration of **7** by the X-ray technique.

When the (*Z*)- and (*E*)-diacetates **3** and **4** were irradiated in dioxane or i-PrOH solution, they remained mostly unchanged (recovery being *ca.* 80% in dioxane and *ca.* 70% in i-PrOH, while the rest was a complex mixture). On the other hand, similarly to **1** and **2**, irradiation of **3** and **4** in acetone solution produced, besides (*Z*/*E*)- (or (*E*/*Z*)-) isomerization, *i*) epoxidation (only in the presence of air) affording *cis*-oxirane **8** ((1*S*,10*R*); from (*Z*)-isomer **3**) and both *trans*-oxiranes **9** and **10** ((1*S*,10*S*) and (1*R*,10*R*), resp.; from (*E*)-isomer **4**) in 7 and 17% yield, respectively, and *ii*) acetone addition to the olefinic double bond giving an unresolvable mixture of the (1*R*)- and (1*S*)-acetonyl derivatives **11a** and **11b** in 8% yield (results in *Table 2*).

To confirm the structures of the epoxides **8**–**10**, the diacetates **3** and **4** were separately treated with 3-chloroperbenzoic acid, to give *cis*-epoxide **8** (quant.; from **3**) and both diastereoisomeric *trans*-epoxides **9** and **10** (39 and 50% yield, resp.; from **4**), respectively.

Scheme 2

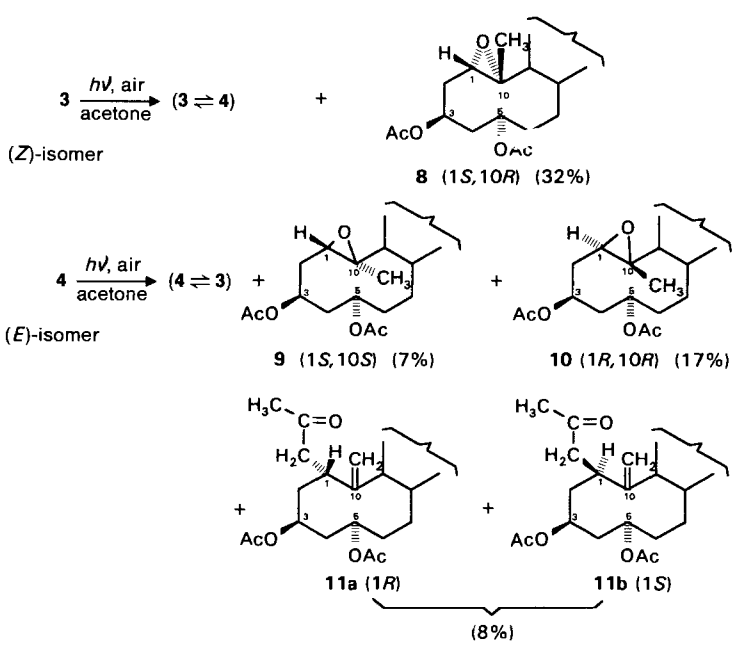

Table 2. *Irradiation of* **3** *and* **4** *in Acetone Solution* (*ca.* $2 \cdot 10^{-3}$ M) *with a* TQ-150-Z2 *Lamp for 4 h*

Substrate	Conditions	Yields [%][a]					
		3	**4**	**8**	**9**	**10**	**11a,b**
(*Z*)-Isomer **3**	*hν*, air	36	18	32	–	–	traces[b]
(*E*)-Isomer **4**	*hν*, air	21	9	–	7	17	8
	hν, N_2	34	16	–	–	–	24

[a] All yields (average of at least 3 experiments) refer to crude products, separated by column chromatography on silica gel (yields after recrystallization or rechromatography were lower by 10–15%).

[b] Eluted as a mixture with some other unidentified photoproducts.

The distinction between **9** and **10** was possible on the basis of their ^{1}H- and ^{13}C-NMR data, and the presence of both (1*R*)- and (1*S*)-acetonyl derivatives **11a** and **11b** was established by IR and ^{1}H-NMR data.

The ^{1}H-NMR signal of H–C(1) in **9** appears at considerably lower field (3.34 ppm) than the corresponding signal of the stereoisomeric analogue **10** (2.82 ppm). According to molecular models, H–C(1) of **9** is exposed to the deshielding influence of the 3β-AcO group, implying that this oxirane has the (1*S*,10*S*)-configuration and, therefore, **10** the (1*R*,10*R*)-configuration. In accordance with the proposed configurations, the ^{13}C-NMR signal for Me(19) of **9** appears at 23.3 ppm (characteristic of an α-oriented secosteroidal Me(19) group [5] [6]) and the corresponding signal of **10** at 13.5 ppm (characteristic of a β-oriented Me group [6]).

The acetonyl mixture **11a**/**11b** shows double peaks for the exocyclic CH_2 group in the IR (1640 and 1630 cm^{-1}) and in the ^{1}H-NMR (4.90 and 4.95 (2*s*) ppm and 5.10 and 5.12 (2*s*) ppm) and for the acetonyl group in the ^{1}H-NMR (2.12 and 2.18 (2*s*)).

To get more information regarding the mechanism of epoxidation, an O_2-saturated benzene/MeOH 9:1 solution of (*E*)-isomer **2** was irradiated in the presence of methylene blue or eosine, dyes which are known to be sensitizers for singlet oxygen. However, both proved to be inefficient in inducing epoxidation, indicating that the reaction does not proceed by the intermediacy of singlet oxygen. Rather, all the results obtained suggest that acetone used as solvent plays an active role in the photoepoxidation process.

A plausible mechanistic and stereochemical course for photoepoxidation (*Scheme 3*) would consist in the primary formation of a biradical intermediate **A**[5]), arising from attack of acetone triplet at C(1) of the olefinic (*Z*)- or (*E*)-double bond in compounds **1**–**4**. It seems that the stereochemistry of acetone approach to this double bond is determined by the ground-state conformations of the respective molecules in solution. Namely, ^{1}H-NMR and ^{13}C-NMR studies showed [7] that the (*Z*)- and (*E*)-acetates **1** and **2** and (*Z*)-diacetate **3** exist in solution in only one conformation, from which intermediates (*Z*)-**A** and (*E*)-**A**, respectively, can be derived, while the (*E*)-diacetate **4** exists in solution in two conformational forms (with differently oriented 1(10)-double bond), from which intermediates (*E*)-**A** and (*E*)′-**A** can be expected. The next step in the photoepoxidation involves attachment of molecular O_2 (in its triplet state) to the C(10) radical site of the original 1(10)-double bond, to give peroxy biradicals (*Z*)-**B**, (*E*)-**B**, and (*E*)′-**B**, respectively. Biradicals of type **A** and **B** closely resemble the species which *Shimizu* and *Bartlett* considered as possible intermediates in the photoepoxidation of alkenes sensitized by α-diketones and benzophenone [8]. However, in contrast to photoepoxidation of alkenes described by these authors, which leads exclusively to *trans*-epoxides from either (*Z*)- or (*E*)-alkenes (indicating that the reaction proceeds *via* a freely rotating intermediate), photoepoxidation of the 1(10)-double bond in **1**–**4** requires non-flexible biradical intermediates in which the geometry of the starting molecules is preserved. According to the mechanism proposed by *Shimizu* and *Bartlett* [8] the peroxy biradicals (*Z*)-**B**, (*E*)-**B**, and (*E*)′-**B** could finally fragment to give the epoxides **5**, **6**, and **8**–**10** and a biradical species **C** possessing a methylene dioxide structure[6]).

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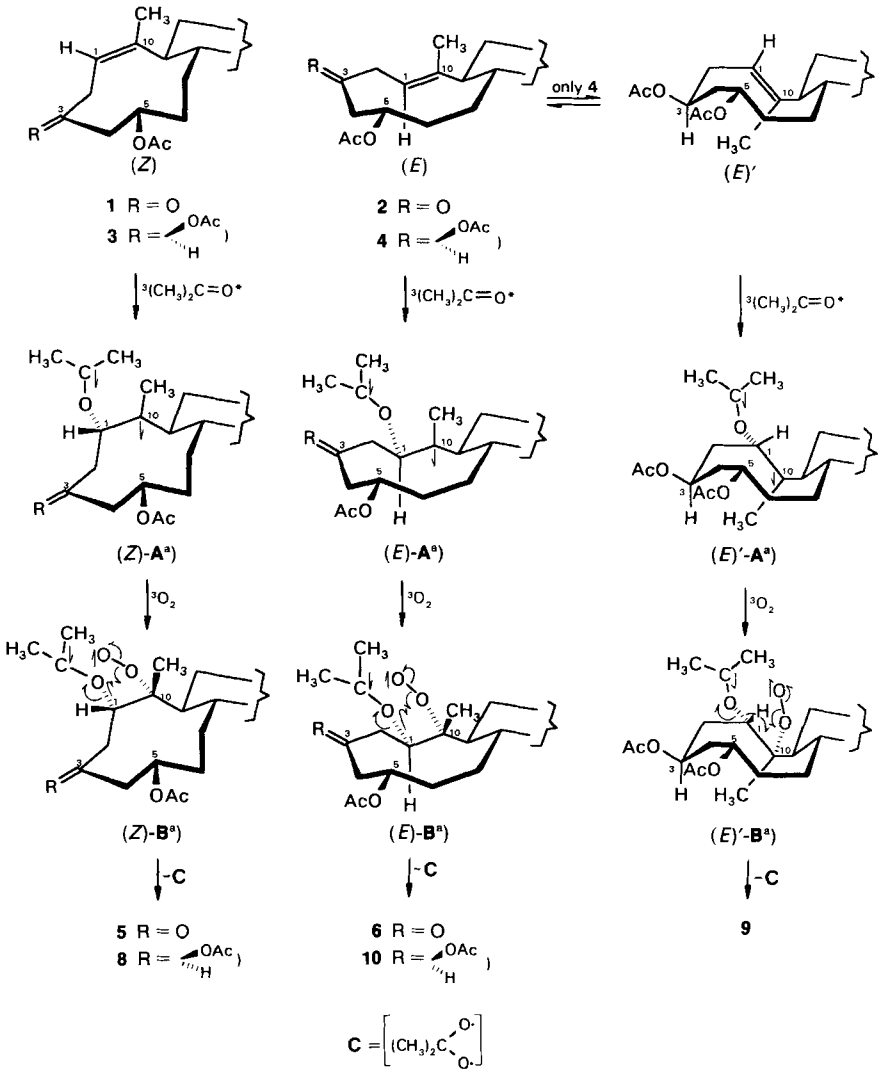
[5]) Biradicals of type **A** are usually intermediates in the *Paterno-Büchi* reaction. However, in the present case, O-addition at C(10) is preferred to intramolecular biradical coupling, probably because strong steric repulsion between the acetone Me groups and the 2 H–C(11) prevents ring closure to oxetane structure.

[6]) It was suggested [8] that biradical **C** could eventually dimerize to a cyclic peroxide, which might fragment photochemically to produce acetone and molecular O_2.

Scheme 3

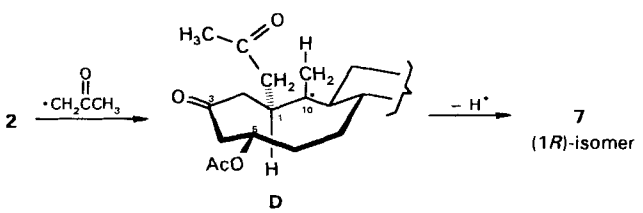


[a]) The prefixes (*Z*), (*E*), and (*E*)′ of **A** and **B** refer to the configuration of the starting material.

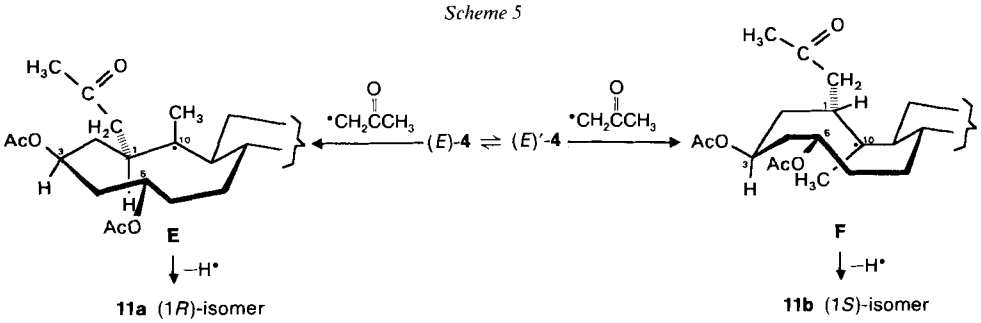
On the other hand, the oxidative addition of acetone to the 1(10)-double bond of 5,10-secosteroids, with formation of a new C–C bond, can be rationalized as a free-radical process in which the acetonyl radical is involved[7]) (*Scheme 4*). This species could add to C(1) of the (*E*)-double bond of **2** to produce a radical **D**. H-Elimination from this radical results in stereospecific formation of the 1(10)-unsaturated (1*R*)-acetonyl deriva-

[7]) The ESR spectra of $MeCOCH_2^{\cdot}$ and $Me_2\dot{C}(OH)$ radicals were recorded during UV irradiation of liquid acetone, indicating H-transfer from unexcited to photochemically excited molecules [9].

Scheme 4



Scheme 5



tive **7**. Although radicals of type **D**, generated photochemically or thermally from ketone and cyclic or terminal alkenes, are known to stabilize by H-addition to give the corresponding saturated carbonyl compounds [10] [11], the sterically hindered C(10) radical **D** behaves differently. Probably, due to steric reasons, H-abstraction from the more accessible Me(19) group (presumably by triplet acetone[8])) rather than H-abstraction by the C(10) radical from, *e.g.*, unexcited acetone molecules, is the preferable way of its stabilization.

The (*E*)-diacetate **4**, which exists in solution in two conformations ((*E*) and (*E*)′) [7], could give with the acetonyl radical two configurationally different species **E** and **F** (*Scheme 5*). Their stabilization (by H-elimination) would lead to the diastereoisomeric (1*R*)- and (1*S*)-acetonyl derivatives **11a** and **11b**, respectively, both, as described above, being formed upon photolysis of the (*E*)-diacetate **4** in acetone solution (*Scheme 2*, *Table 2*).

The authors are grateful to the *Serbian Academy of Sciences and Arts* and to the *Serbian Research Found* for financial support.

Experimental Part[9])

1. *General.* Removal of solvents was carried out under reduced pressure. Light petroleum ether refers to the fraction boiling at 40–60°. Column chromatography (CC): silica gel 0.063–0.200 mm. TLC: control of reactions and separation of products on silica gel *G* (*Stahl*) with benzene/AcOEt 18:1 or 9:1; detection with 50% aq. H_2SO_4 soln. M.p.: uncorrected. IR Spectra: *Perkin-Elmer-337* spectrophotometer; $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *Varian AH-100* or *Bruker AM-360* (^1H at 100 or 360 MHz, ^{13}C at 25.15 or 90.55 MHz); $CDCl_3$ soln. at r.t.; TMS as internal standard; δ in ppm, J in Hz. Mass Spectra: *Finnigan-MAT 8320*.

[8]) Hydroxy radicals thus formed could give pinacol as a photochemical product.

[9]) IR, routine ^1H-NMR, and elemental microanalyses were carried out in the Laboratories for Instrumental Analysis of the Faculty of Chemistry, Belgrade. NMR Measurements were performed at *Ciba-Geigy Ltd.*, Basel, Switzerland.

2. *(Z)-3-Oxo-5,10-secocholest-1(10)-en-5α-yl Acetate* [1] (**1**): M.p. 141–142° acetone/MeOH). $[\alpha]_D^{20} = +82$.
(E)-3-Oxo-5,10-secocholest-1(10)-en-5α-yl Acetate [1] (**2**): M.p. 140–141° (acetone/MeOH). $[\alpha]_D^{20} = +195$.
(Z)-5,10-Secocholest-1(10)-ene-3β,5α-diyl Diacetate [3] (**3**): M.p. 86–87° (MeOH). $[\alpha]_D^{20} = +52$.
(E)-5,10-Secocholest-1(10)-ene-3β,5α-diyl Diacetate [3] (**4**): M.p. 95–96° (acetone/MeOH). $[\alpha]_D^{20} = -18$.

3. *UV Irradiation of* **1–4**. *General Procedure*. At r.t. and with stirring, solns. of **1–4** (230–250 mg) in dioxane, i-PrOH, or acetone (260 ml) were irradiated 4 h in a cylindric flask with a high-pressure mercury lamp (*TQ 150 Z2*) contained in a H_2O-cooled jacket of *Pyrex*. In some experiments performed with **1** and **2** in acetone (*Table 1*), O_2 or N_2 was bubbled through the soln. After irradiation and evaporation, the residue obtained upon UV irradiation in acetone was diluted with Et_2O, the org. layer washed with sat. aq. $NaHCO_3$ soln. and H_2O, dried (Na_2SO_4), and evaporated. All resulting mixtures were separated by CC (silica gel (15 g), benzene/Et_2O in various proportions).

CC Separation of Irradiation Mixtures from **1** *and* **2**. Benzene/Et_2O 99:1 eluted **2**, benzene/Et_2O 98:2 **1**, benzene/Et_2O 97:3 **5**/**6**, and benzene/Et_2O 95:5 and 94:6 **7**. Fractions eluted with Et_2O contained complex mixtures which were not further investigated.

CC Separation of Irradiation Mixtures from **3** *and* **4**. Benzene/Et_2O 99:1 gave **4**, benzene/Et_2O 98:2 **3**, benzene/Et_2O 97:3 **9**, followed by **10** (from **4**) or **8** (from **3**), and benzene/Et_2O 92:8 **11a**/**11b**. Benzene/Et_2O 9:1 and 1:1 and Et_2O eluted a complex mixture, from which no defined products could be isolated or identified.

(1S,10R)-1,10-Epoxy-3-oxo-5,10-secocholestan-5α-yl Acetate (**5**). M.p. 123–124° (acetone/MeOH). $[\alpha]_D^{20} = +20.3$ ($c = 0.54$, $CHCl_3$). IR (KBr): 1734*s*, 1714*s*, 1240*s*, 1022*s*, 965*m*, 755*w*. ^{1}H-NMR (360 MHz): 0.70 (*s*, Me(18)); 0.86 (*d*, Me(26), Me(27)); 0.91 (*d*, Me(21)); 1.24 (*s*, Me(19)); 2.04 (*s*, AcO); 2.64–2.84 (*m*, H_α–C(2), CH_2(4)); 2.92 (*dd*, $J_{gem} = 17.5$, $J(1\beta,2\beta) = 4$, H_β–C(2)); 3.31 (*dd*, $J(1\beta,2\alpha) = 11.5$, $J(1\beta,2\beta) = 4$, H_β–C(1)); 4.72 (*m*, H_β–C(5)). ^{13}C-NMR (25.15 MHz): 207.2 (*s*, C(3)); 170.3 (*s*, MeCOO); 72.2 (*d*, C(5)); 68.8 (*s*, C(10)); 62.6 (*d*, C(1)); 56.4 (*d*, C(17)); 51.2 (*d*, C(14)); 48.8 (*t*, C(4)); 44.3 (*d*, C(9)); 43.1 (*s*, C(13)); 40.9 (*t*, C(12)); 40.0 (*t*, C(24)); 39.4 (*t*, C(2)); 36.6 (*d*, C(8)); 36.3 (*t*, C(22)); 36.1 (*d*, C(20)); 29.1 (*t*, C(6)); 28.5 (*d*, C(25)); 28.3 (*t*, C(16)); 24.9 (*t*, C(15)); 24.7 (*t*, C(11)); 24.2 (*t*, C(23)); 23.6 (*t*, C(7)); 23.3 (*q*, C(27)); 23.0 (*q*, C(26)); 21.7 (*q*, *Me*COO); 19.2 (*q*, C(19)); 18.7 (*q*, C(21)); 12.2 (*q*, C(18)). Anal. calc. for $C_{29}H_{48}O_4$ (460.703): C 75.61, H 10.50; found: C 75.38, H 10.27.

(1R,10R)-1,10-Epoxy-3-oxo-5,10-secocholestan-5α-yl Acetate (**6**). M.p. 147–148° (acetone/MeOH). $[\alpha]_D^{20} = +65.2$ ($c = 0.95$, $CHCl_3$). IR (KBr): 1740*s*, 1720*s*, 1240*s*, 1030*m*, 970*w*, 760*w*. ^{1}H-NMR (360 MHz): 0.70 (*s*, Me(18)); 0.87 (*d*, Me(26), Me(27)); 0.91 (*d*, Me(21)); 1.21 (*s*, Me(19)); 2.03 (*s*, AcO); 2.31 (*dd*, $J_{gem} = 16$, $J(1\alpha,2\beta) = 11$, H_β–C(2)); 2.61 (*dd*, $J_{gem} = 15$, $J(4\beta,5\beta) = 5$, H_β–C(4)); 3.14 (*dd*, $J_{gem} = 16$, $J(1\alpha,2\alpha) = 5$, H_α–C(2)); 3.14 (*dd*, $J_{gem} = 15$, $J(4\alpha,5\beta) = 10$, H_α–C(4)); 3.43 (*dd*, $J(1\alpha,2\beta) = 11$, $J(1\alpha,2\alpha) = 5$, H_α–C(1)); 5.24 (*m*, H_β–C(5)). ^{13}C-NMR (25.15 MHz): 204.9 (*s*, C(3)); 169.8 (*s*, MeCOO); 71.3 (*d*, C(5)); 62.2 (*s*, C(10)); 60.2 (*d*, C(1)); 56.3 (*d*, C(17)); 54.9 (*d*, C(14)); 54.7 (*d*, C(9)); 45.9 (*t*, C(4)); 42.9 (*t*, C(2)); 42.9 (*s*, C(13)); 39.5 (*t*, C(12)); 39.0 (*t*, C(24)); 38.4 (*d*, C(8)); 36.1 (*t*, C(22)); 24.6 (*t*, C(7)); 24.3 (*t*, C(11)); 23.8 (*t*, C(15)); 23.8 (*t*, C(23)); 22.8 (*q*, C(27)); 22.6 (*q*, C(26)); 21.0 (*q*, *Me*COO); 18.7 (*q*, C(21)); 12.5 (*q*, C(18)); 12.0 (*q*, C(19)). Anal. calc. for $C_{29}H_{48}O_4$ (460.703): C 75.61, H 10.50; found: C 75.73, H 10.60.

(1R)-1-Acetonyl-3-oxo-5,10-secocholest-10(19)-en-5α-yl Acetate (**7**). M.p. 144–145° (acetone/MeOH). $[\alpha]_D^{20} = +37.5$ ($c = 0.56$, $CHCl_3$). IR (CH_2Cl_2): 3050*w*, 1730*s*, 1640*w*, 1245*s*, 1030*m*, 910*m*. ^{1}H-NMR (360 MHz): 0.71 (*s*, Me(18)); 0.88 (*d*, Me(26), Me(27)); 0.90 (*d*, Me(21)); 2.03 (*s*, AcO); 2.17 (*s*, COMe); 2.38–2.72 (*m*, H_α–C(1), CH_2(2), CH_2(4)); 2.97, 3.10 (2 br. *m*, CH_2CO); 5.00, 5.02 (2 *s*, CH_2(19)); 5.01 (*m*, H_β–C(5)). ^{13}C-NMR (90.55 MHz): 208.4 (*s*, *C*OMe); 207.1 (*s*, C(3)); 170.1 (*s*, Me*C*OO); 155.0 (*s*, C(10)); 110.8 (*t*, C(19)); 71.5 (*d*, C(5)); 56.4 (*d*, C(17)); 52.8 (*d*, C(14)); 50.2 (*d*, C(9)); 49.8 (*t*, C(4)); 49.8 (*t*, *C*H$_2$CO); 44.1 (*t*, C(2)); 42.8 (*s*, C(13)); 40.1 (*d*, C(1)); 40.1 (*t*, C(12)); 39.5 (*t*, C(24)); 36.1 (*t*, C(22)); 35.7 (*d*, C(8)); 35.7 (*d*, C(20)); 31.9 (*t*, C(6)); 30.7 (*q*, CO*Me*); 29.7 (*t*, C(7)); 28.0 (*d*, C(25)); 27.9 (*t*, C(16)); 24.3 (*t*, C(15)); 23.8 (*t*, C(23)); 23.0 (*t*, C(11)); 22.8 (*q*, C(27)); 22.6 (*q*, C(26)); 21.3 (*q*, *Me*COO); 18.6 (*q*, C(21)); 11.9 (*q*, C(18)). MS: 500 (M^+), 440 ([500 – 60]$^+$), 425 ([440–15]$^+$), 382 ([440–58]$^+$). Anal. calc. for $C_{32}H_{52}O_4$ (500.768): C 76.75, H 10.47; found: C 76.66, H 10.31.

(1S,10R)-1,10-Epoxy-5,10-secocholestane-3β,5α-diyl Diacetate (**8**). M.p. 146–147° (MeOH). $[\alpha]_D^{20} = +24.8$ ($c = 1.00$, $CHCl_3$). IR (KBr): 1740*s*, 1245*s*, 1210*m*, 1020*m*, 865*w*, 800w. ^{1}H-NMR (360 MHz): 0.72 (*s*, Me(18)); 0.88 (*d*, Me(26), Me(27)); 0.92 (*d*, Me(21)); 1.28 (*s*, Me(19)); 2.05, 2.08 (2*s*, 2 AcO); 3.03 (*d*, $J(1\beta,2\beta) = 11$, H_β–C(1)); 4.92 (*m*, H_β–C(5)); 5.31 (*m*, H_α–C(3)). ^{13}C-NMR (90.56 MHz): 170.2, 169.8 (2*s*, 2 MeCOO); 70.9 (*d*, C(5)); 67.6 (*d*, C(3)); 64.0 (*s*, C(10)); 61.8 (*d*, C(1)); 56.2 (*d*, C(17)); 51.6 (*d*, C(14)); 43.0 (*s*, C(13)); 41.1 (*d*, C(9)); 39.5 (*t*, C(24)); 39.4 (*t*, C(12)); 36.8 (*d*, C(8)); 36.1 (*t*, C(22)); 35.7 (*d*, C(20)); 32.5 (*t*, C(4)); 31.3 (*t*, C(2)); 28.0 (*t*, C(16)); 28.0 (*d*, C(25)); 24.1 (*t*, C(15)); 23.9 (*t*, C(6)); 23.7 (*t*, C(11)); 23.6 (*t*, C(23)); 22.8 (*t*, C(11)); 23.6 (*t*, C(23)); 22.8 (*t*, C(7)); 22.8 (*q*, C(27)); 22.6 (*q*, C(26)); 21.4, 21.1 (2*q*, 2 *Me*COO); 18.7 (*q*, C(21)); 18.4 (*q*, C(19)); 12.1 (*q*, C(18)). Anal. calc. for $C_{31}H_{52}O_5$ (504.757): C 73.77, H 10.38; found: C 73.82, H 10.24.

(1S,10S)-1,10-Epoxy-5,10-secocholestane-3β,5α-diyl Diacetate (**9**). M.p. 129–131° (acetone/MeOH). $[\alpha]_D^{20} = +20.6$ ($c = 0.65$, $CHCl_3$). IR (KBr): 1730*s*, 1720*s*, 1245*s*, 1230*s*, 1035*m*, 1015*m*, 885*w*, 780*w*. ^{1}H-NMR (360 MHz): 0.68 (*s*, Me(18)); 0.86 (*d*, Me(26), Me(27)); 0.90 (*d*, Me(21)); 1.40 (*s*, Me(19)); 2.00, 2.07 (2*s*, 2 AcO); 3.34 (*dd*, $J(1\beta,2\alpha) = 12$, $J(1\beta,2\beta) = 2$, H_β–C(1)); 5.24, 5.32 (2*m*, H_α–C(3), H_β–C(5)). ^{13}C-NMR (90.56 MHz): 170.3, 170.1 (2*s*, 2 Me*C*OO); 69.0 (*d*, C(5)); 66.2 (*d*, C(3)); 64.0 (*s*, C(10)); 57.1 (*d*, C(17)); 56.1 (*d*, C(1)); 56.1 (*d*, C(14)); 49.7 (*d*, C(9)); 43.0 (*s*, C(13)); 39.5 (*t*, C(24)); 39.4 (*t*, C(12)); 37.0 (*d*, C(8)); 36.7 (*t*, C(4)); 36.1 (*t*, C(22)); 35.7 (*d*, C(20)); 33.5 (*t*, C(2)); 32.6 (*t*, C(6)); 28.7 (*t*, C(7)); 28.0 (*t*, C(16)); 28.0 (*d*, C(25)); 24.6 (*t*, C(15)); 23.8 (*t*, C(23)); 23.5 (*t*, C(11)); 23.3 (*q*, C(19)); 22.8 (*q*, C(27)); 22.6 (*q*, C(26)); 21.2, 21.1 (2*q*, 2 *Me*COO); 18.7 (*q*, C(21)); 12.0 (*q*, C(18)). Anal. calc. for $C_{31}H_{52}O_5$ (504.757): C 73.77, H 10.38; found: C 77.53, H 10.62.

(1R,10R)-1,10-Epoxy-5,10-secocholestane-3β,5α-diyl Diacetate (**10**). M.p. 109–110° (MeOH). $[\alpha]_D^{20} = +7.1$ ($c = 0.5$, $CHCl_3$). IR (KBr): 1735*s*, 1730*s*, 1245*s*, 1210*m*, 1020*m*, 865*w*, 665*w*. ^{1}H-NMR (360 MHz): 0.71 (*s*, Me(18)); 0.87 (*d*, Me(26), Me(27)); 0.91 (*d*, Me(21)); 1.27 (*s*, Me(19)); 2.03, 2.05 (2*s*, 2 AcO); 2.82 (*d*, $J(1\alpha,2\beta) = 11$, H_α–C(1)); 4.98 (*m*, H_β–C(5)); 5.25 (*m*, H_α–C(3)). ^{13}C-NMR (90.56 MHz): 170.4, 169.8 (2*s*, 2 Me*C*OO); 70.3 (*d*, C(5)); 68.6 (*d*, C(3)); 63.3 (*s*, C(10)); 62.9 (*d*, C(1)); 56.2 (*d*, C(17)); 54.4 (*d*, C(14)); 52.7 (*d*, C(9)); 43.3 (*s*, C(13)); 39.8 (*t*, C(12)); 39.5 (*t*, C(24)); 38.0 (*d*, C(8)); 36.1 (*t*, C(22)); 35.8 (*d*, C(20)); 34.8 (*t*, C(4)); 31.6 (*t*, C(6)); 28.6 (*t*, C(7)); 28.0 (*d*, C(25)); 27.8 (*t*, C(16)); 24.9 (*t*, C(2)); 24.5 (*t*, C(15)); 23.8 (*t*, C(23)); 23.6 (*t*, C(11)); 22.8 (*q*, C(27)); 22.6 (*q*, C(26)); 21.3, 21.2 (2*q*, 2 *Me*COO); 18.7 (*q*, C(21)); 13.5 (*q*, C(19)); 12.1 (*q*, C(18)). Anal. calc. for $C_{31}H_{52}O_5$ (504.757): C 73.77, H 10.38; found: C 73.68, H 10.25.

(1R)/(1S)-1-Acetonyl-5,10-secocholest-10(19)-ene-3β,5α-diyl Diacetate (**11a**/**11b**). Oil. IR (CCl_4): 3060*w*, 1730*s*, 1710*s*, 1640*w*, 1630*w*, 1250*s*, 1010*s*. ^{1}H-NMR (100 MHz): 0.70, 0.73 (parts of 2*s*, 3 H, Me(18)); 0.86 (*d*, 6 H, Me(26), Me(27)); 0.89 (*d*, 3 H, Me(21)); 1.98, 2.02, 2.03, 2.05 (parts of 4*s*, 6 H, 2 AcO): 2.12, 2.18 (parts of 2*s*, 3 H, COMe); 4.90, 4.95, 5.10, 5.12 (parts of 4*s*, 2 H, CH_2(19)); 4.80, 5.25 (parts of br. *m*, 2 H, H_α–C(3), H_β–C(5)).

4. *Epoxidation with 3-Chloroperbenzoic Acid.* 4.1. To a stirred soln. of **1** (100 mg) in CH_2Cl_2 (5 ml) cooled to 0°, 3-chloroperbenzoic acid (85%; 50 mg) was added, and the mixture allowed to warm to r.t. After 1 h, it was diluted with Et_2O, the org. layer washed with H_2O, 10% aq. KI soln., aq. $Na_2S_2O_3$ soln., H_2O, sat. aq. $NaHCO_3$ soln., and H_2O, dried (Na_2SO_4), and evaporated. The residue (105 mg) was recrystallized from acetone/MeOH to give **5** (96 mg, 92.7%). M.p. 123–124° (undepressed by admixture of the sample obtained in the photoepoxidation). Spectral data: identical to those reported above.

4.2. Compound **2** (100 mg) in CH_2Cl_2 (5 ml) was treated with 3-chloroperbenzoic acid (85%; 50 mg) for 2 h as above. The solid (102 mg) obtained after usual workup was recrystallized from acetone/MeOH: **6** (93 mg, 89.8%). M.p. 146–147°. Identical with the photoepoxidation product **6**.

4.3. A soln. of **3** (100 mg) in CH_2Cl_2 (5 ml) was treated with 3-chloroperbenzoic acid (*ca.* 90%; 50 mg) for 6 h as above. Usual workup afforded a crystalline solid (104 mg), which was recrystallized from MeOH: **8** (91 mg, 88.1%). M.p. 146° (undepressed by admixture of **8** obtained in the photoepoxidation).

4.4. A soln. of **4** (200 mg) in CH_2Cl_2 (10 ml) was treated with 3-chloroperbenzoic acid (*ca.* 90%; 100 mg) for 4 h as above. The mixture obtained after usual workup was separated by CC (SiO_2 (12 g)): 81 mg (39.2%) of **9** and 103 mg (49.9%) of **10**. Spectral data: identical to those reported for **9** and **10** above.

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