Photoinduced Molecular Transformations. Part 134.[1] Photoinduced Stereospecific Addition of Methanol to 5β-Cholest-1-en-3-one Oxime and Photoinduced Deconjugation of its 1-Methyl Derivative involving Stereospecific Proton Transfer

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Irradiation of 5β-cholest-1-en-3-one oxime **14** in methanol gave 1α-methoxy-5β-cholestan-3-one oxime **16**, arising from the photoaddition of methanol to the double bond of the enone oxime. 1α-Methoxy-5β-cholestan-3-one **17** as well as 10β-methoxy-5(10→1)*abeo*-1β(H),5β,10α(Me)-cholestan-3-one **15**, arising from a skeletal rearrangement of 5β-cholest-1-en-3-one (generated from the oxime), were the accompanying products in this photoreaction. Deuterium-labelling studies confirmed that the formation of 1α-methoxy-5β-cholestan-3-oxime **16** involves a stereospecific *syn* addition of methanol to the photogenerated, twisted, ground-state double bond of the oximes **B** from the rear side of the steroidal framework.

Irradiation of 1-methyl-5β-cholest-1-en-3-one oxime **23** in methanol, on the other hand, gave almost exclusively 1-methylene-5β-cholestan-3-one oxime **24**, arising from photodeconjugation of the α,β-double bond to the β,γ-position. A deuterium-labelling study established that deuterium is stereospecifically introduced at the 2β-position of 1-methyl-5β-cholest-1-en-3-one oxime **23** in the photodeconjugation in methanol[^{2}H]ol while deuterium is stereospecifically introduced at the 2α-position in the photodeconjugation of its 5α-isomer **6**. These results are fully consistent with our previously proposed pathway concerning the photodeconjugation of 1-methyl-5α-cholest-1-en-3-one oxime **6**; the stereospecific addition of a proton to the photogenerated, twisted double bond of the oxime **D** from the rear side of the steroidal framework was followed by the loss of a proton from the 1-methyl group of the resulting carbocation intermediate. Neither the isoxazole derivative, a product in the photoreaction of 5α-cholest-1-en-3-one oxime **1**, nor the unsaturated lactam from a photo-Beckmann rearrangement was formed in the photoreactions of either 5β-cholest-1-en-3-one oxime **14** or its 1-methyl derivative **23**.

In previous papers,[1,2] we reported on several unprecedented photoreactions of steroidal α,β-unsaturated oximes, such as photorearrangements to an isoxazole derivative or to the β,γ-isomer involving a stereospecific proton transfer, as well as a stereospecific addition of methanol to the α,β-double bond of the oximes. Thus, the irradiation of 5α-cholest-1-en-3-one oxime **1** in methanol gave 4′,5′-dihydroisoxazolo[4′,3′:1,2]-4-nor-1α,5α-cholestane **2** and 1β-methoxy-5α-cholestan-3-one oxime **3**.[2]

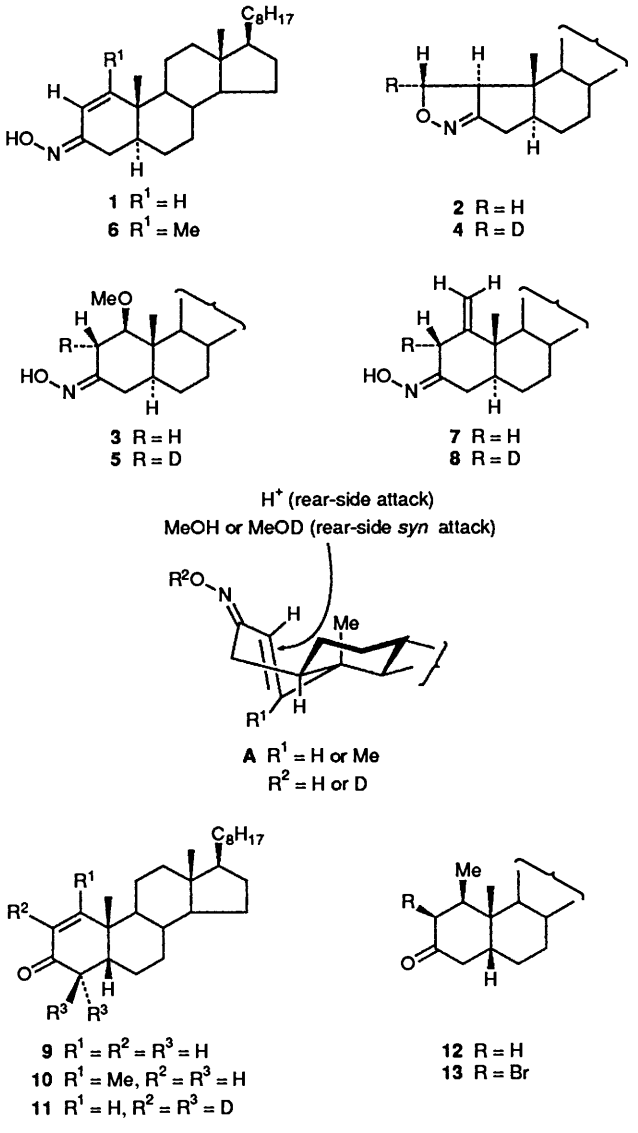
Deuterium-labelling studies of these photoreactions of enone oxime **1** in methanol[^{2}H]ol established that a deuterium or methan[^{2}H]ol is stereospecifically introduced to give 5′α-deuterioisoxazole **4** and 2α-deutero-1β-methoxy-5α-cholestan-3-one oxime **5**.[2] We subsequently found that irradiation of β-methyl-α,β-unsaturated oxime **6** in methanol resulted in an unprecedented isomerization to the β,γ-unsaturated isomer **7**.[1] Deuterium-labelling studies again established that a deuterium is stereospecifically introduced at the 2α-position of steroid oxime **6** to give β,γ-enone oxime **8** from excited α,β-enone oxime **6**.[1] We proposed that the pathways for the formation of the isoxazoles (**2** and **4**), and the β,γ-unsaturated oximes (**7** and **8**) involved a stereospecific protonation (or a deuteronation) at C-2 of a photogenerated, twisted, ground-state intermediate **A** from the rear side of the steroidal framework while the pathway for the formation of methanol adducts (**3** and **5**) involved a stereospecific *syn* addition of methanol to the reactive double bond of intermediate **A**.

Following these investigations, we have now examined the photoreactions of the 5β-isomer **14** of 5α-cholest-1-en-3-one oxime **1** as well as the 5β-isomer **23** of 1-methyl-5α-cholest-1-en-3-one oxime **6**, in order to obtain knowledge concerning the effects of an alteration of the *trans* ring fusion of enone oximes **1** and **6** to *cis* fusion on the stereochemistry of these photoreactions.

We have found that irradiation of 5β-cholest-1-en-3-one oxime **14** with UV light produces products which arise from a stereospecific photoaddition of methanol and new photorearrangement of the photogenerated parent ketone. However, no isoxazole derivative, a product in the photoreaction of the 5α-isomer, was formed. We have also found that the photoreaction of 1-methyl-5β-cholest-1-en-3-one oxime **23** resulted in photoisomerization to the β,γ-isomer, as was also found in the 5α-series. A proton was again stereospecifically introduced at the 2β-position of the β,γ-isomer in this photodeconjugation. We report here our results in full.

Results

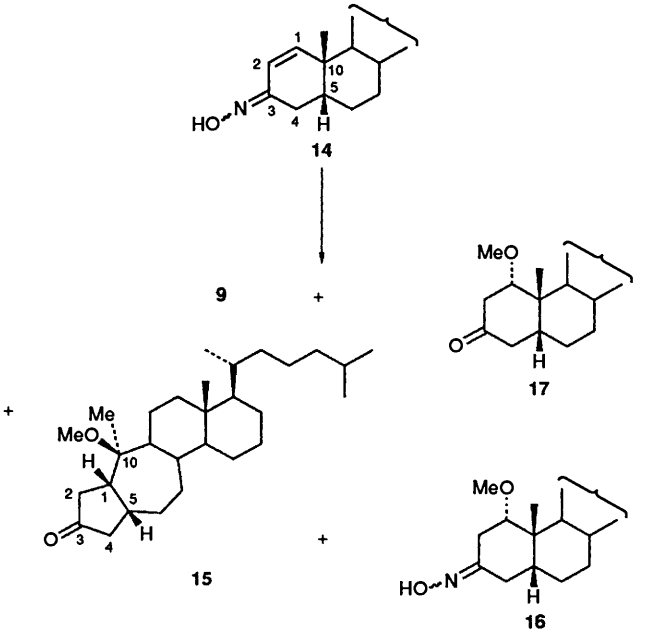
Preparation of the Substrates.—Of the three parent ketones (5β-cholest-1-en-3-one **9**, 1-methyl-5β-cholest-1-en-3-one **10**, and 2,4,4-trideuterio-5β-cholest-1-en-3-one **11**) used to prepare three enone oximes (**14**, **18** and **23**) as substrates, only enone **9** has been described in the literature.[3] Enone **9** for the present experiment was prepared by modification of some of these methods:[3e,f] selective elimination of hydrogen bromide from 2β,4β-dibromo-5β-cholestan-3-one,[4] obtained by bromination of 5β-cholestan-3-one[4] with pyridine hydrobromide perbromide,[5] with calcium carbonate in *N,N*-dimethylacetamide (DMA) (a procedure used by Joly and Warnant[6]) gave 4β-bromo-5β-cholest-1-en-3-one. Reductive removal of the 4β-bromine with tributyltin hydride–azoisobutyronitrile (AIBN) afforded 5β-cholest-1-en-3-one **9**. Conjugate addition of a



methyl group to enone **9** with lithium dimethylcuprate[7] in diethyl ether at room temperature gave 1β-methyl-5β-cholestan-3-one **12** in 96.2% yield. The configuration of the 1-methyl group was assigned as β by a nuclear Overhauser enhancement (NOE) study of its C-2-brominated compound **13** (*vide infra*). The result was in agreement with that for the methylation of 5β-pregn-1-en-3-one with this reagent (previously reported[8]). The bromination of 1β-methyl ketone **12** with pyridine hydrobromide perbromide[5] in glacial acetic acid at room temperature afforded 2,4-dibromo-1β-methyl-5β-cholestan-3-one. Selective removal of the 4-bromine from the 2,4-dibromide with chromium(II) acetate[9] in glacial acetic acid–chloroform gave 2β-bromo-1β-methyl-5β-cholestan-3-one **13**. The yield of bromo ketone **13** from ketone **12** was 81%. The configurations of the 1-methyl and 2-bromo substituents were determined to be β on the basis of NOE measurements; irradiation of a signal (1α-H) (a double quartet) at δ 2.53 resulted in an enhancement of the signal area of a doublet at δ 5.13 ascribable to 2α-H but no enhancement of the signal area at δ 1.08 ascribable to 19-H_3. Conversely, irradiation of the signal (2α-H) at δ 5.13 resulted in an enhancement of the signal at δ 2.53. The elimination of hydrogen bromide from 2β-bromide **13** with calcium carbonate in refluxing DMF gave 1-methyl-5β-cholest-1-en-3-one **10**. The yield from 1β-methyl-5β-cholestan-3-one **12** to the enone **10** was 65.5%.

2,4,4-Trideuterio-5β-cholest-1-en-3-one **11** was prepared by the deuteriation of enone **9** with methan[^{2}H]ol and sodium under reflux for 2 days by the standard method. Oximation of these three steroidal ketones (**9**, **10** and **11**) by the standard method gave in each case a mixture of the respective (*E*)- (*anti*) and (*Z*)-(*syn*) oxime **14**, **23** and **18**.

Photoreactions of Oximes **14** (*Scheme* 1).—Photoreaction of oxime **14** in methanol was carried out with a low-pressure mercury arc generated by a Rayonet RPR photochemical chamber reactor, as described in previous papers.[1,2] A solution of oxime **14** in methanol placed in a quartz vessel was irradiated under nitrogen for 15 h at room temperature to give the parent enone **9** (30.6%) as well as three other products (**15**–**17**) (93.6% conversion) by preparative TLC (PLC).



Scheme 1 *Reagents and conditions:* hν, MeOH

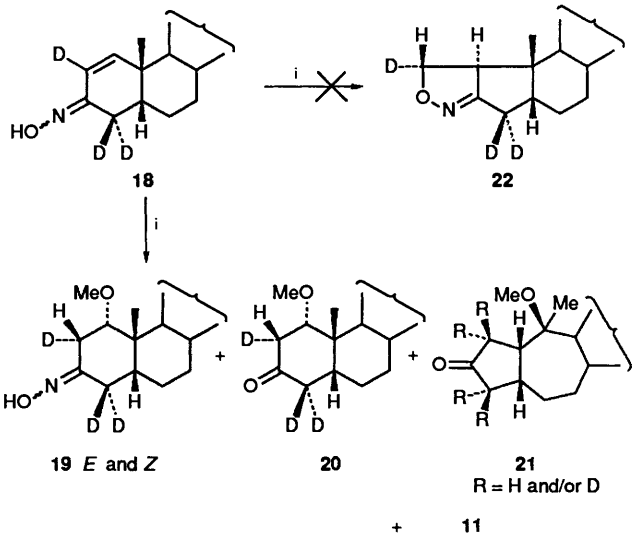
The molecular formula of product **17** (7.1%) was established as $C_{28}H_{48}O_2$ by high-resolution mass spectrometry. The IR spectrum showed the presence of a 6-membered cyclic ketone and the absence of a hydroxy group. The ^{1}H NMR spectrum exhibited a signal due to the methoxy group at δ 3.27. It also exhibited a double doublet signal at δ 2.97 that is assignable to a proton attached to the carbon substituted with a methoxy group. These spectral results indicate that product **17** was 1-methoxy-5β-cholestan-3-one. The configuration of the methoxy group was assigned to be α on the basis of the coupling constants of the double doublet ($J_{1\beta,2\alpha}$ 11.48, $J_{1\beta,2\beta}$ 3.9 Hz) at δ 2.97.

The molecular formula of crystalline product **15** (6.6%) was established as $C_{28}H_{48}O_2$ by both combustion analysis and mass spectrometry. The IR spectrum exhibited a band at 1734 cm^{-1} that is attributable to the carbonyl group in a 5-membered ring. The ^{1}H NMR spectrum (400 MHz) indicated that the product **15** was identical with 10β-methoxy-5(10→1)*abeo*-1β(H),5β,10α(Me)-cholestan-3-one obtained when a solution of 5β-cholest-1-en-3-one **9** in methanol was irradiated with UV light.[10] The details concerning the analysis of the structure of product **15** and its genesis have been reported elsewhere.[10]

The mass, IR and ^{1}H NMR spectral results for product **16** (12.5%) indicated that it was a 1:1 mixture of the *E* and *Z* 1α-methoxy-5β-cholestan-3-one oximes; the EI mass spectrum exhibited a molecular ion at *m*/*z* 431. The IR spectrum indicated the absence of a carbonyl group and the presence of the hydroxyimino group. The ^{1}H NMR spectrum exhibited singlets

at δ 3.30 and 3.33 that are assignable to the methoxy group of the *E*- and *Z*-isomer respectively. It also exhibited a pair of double doublets at δ 2.77 and 2.84, each of which is assignable to the proton attached to the carbon bearing the methoxy group in the *E* and *Z* isomers. The configurations of the methoxy groups, as well as the ratio of the *E* and *Z* isomers in product **16**, were determined by an analysis of the ^{1}H NMR spectrum. Details concerning this analysis are given in the Experimental section.

Photoreaction of Oxime **18** *labelled with Deuterium* (*Scheme* 2).—In order to establish the stereoselectivity of the addition of



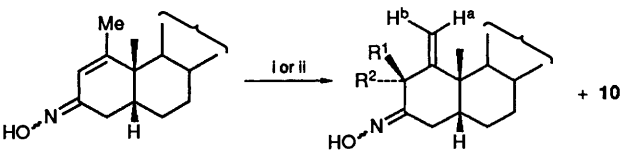
Scheme 2 *Reagents and conditions:* i, *hν*, MeOH

methanol to the enone oxime **14**, the photoreaction of 5β-[2,4,4-$^2H_3$]cholest-1-en-3-one oximes **18** in methanol was carried out. Irradiation of trideuterio oximes **18** in methanol under the above mentioned conditions resulted in an 88% conversion of the oximes, giving a 5:7 mixture of *E*- and *Z*-trideuterio oximes **19** (8.3%), the trideuterio ketone **20** (6.9%), a mixture of deuteriated rearranged ketones **21** (4.4%), and the parent ketone **11** (24.0%). No isoxazolocholestane **22** was formed in this photoreaction. The 400 MHz ^{1}H NMR spectrum of the oxime **19** exhibited a pair of doublets at δ 2.58 and 2.83 (*J* 3.9 Hz) as well as a pair of doublets at δ 2.76 and 3.48 (*J* 3.9 Hz). Since the 1-methoxy group has been shown to be α-oriented, the coupling constants and the chemical shifts of these signals enabled us to assign the former pairs to (*Z*)-2β-H and (*Z*)-1β-H, while the latter pairs were assigned to (*E*)-1β-H and (*E*)-2β-H. Thus, this experiment showed that a deuterium is stereospecifically introduced at the 2α-position of the 5β-steroidal oxime in this photoaddition in methanol.

The ^{1}H NMR spectrum of the trideuterio ketone **20** exhibited a pair of doublets at δ 2.62 and 2.96, both with *J* 3.42 Hz, and a singlet at δ 3.27. These signals can be safely assigned to the 2β-H, 1β-H and 1α-methoxy group, respectively.

The mass and ^{1}H NMR spectra of the rearranged ketone **21** indicated that it was a mixture of the trideuteriated ketone and small amounts of less deuteriated ketones. The formation of these ketones can be explained by successive exchanges of the deuterium attached to the α-position of the carbonyl group by a proton through a photogenerated enol tautomer of the initially formed rearranged ketone.

Photoreaction of 1-*Methyl*-5β-*cholest*-1-*en*-3-*one Oxime* **23** (*Scheme* 3).—Photoreaction of oxime **23** in methanol with a low-pressure mercury arc under the above mentioned conditions for 5 h gave 1-methyl-5β-cholest-1-en-3-one **10** in 21.9%



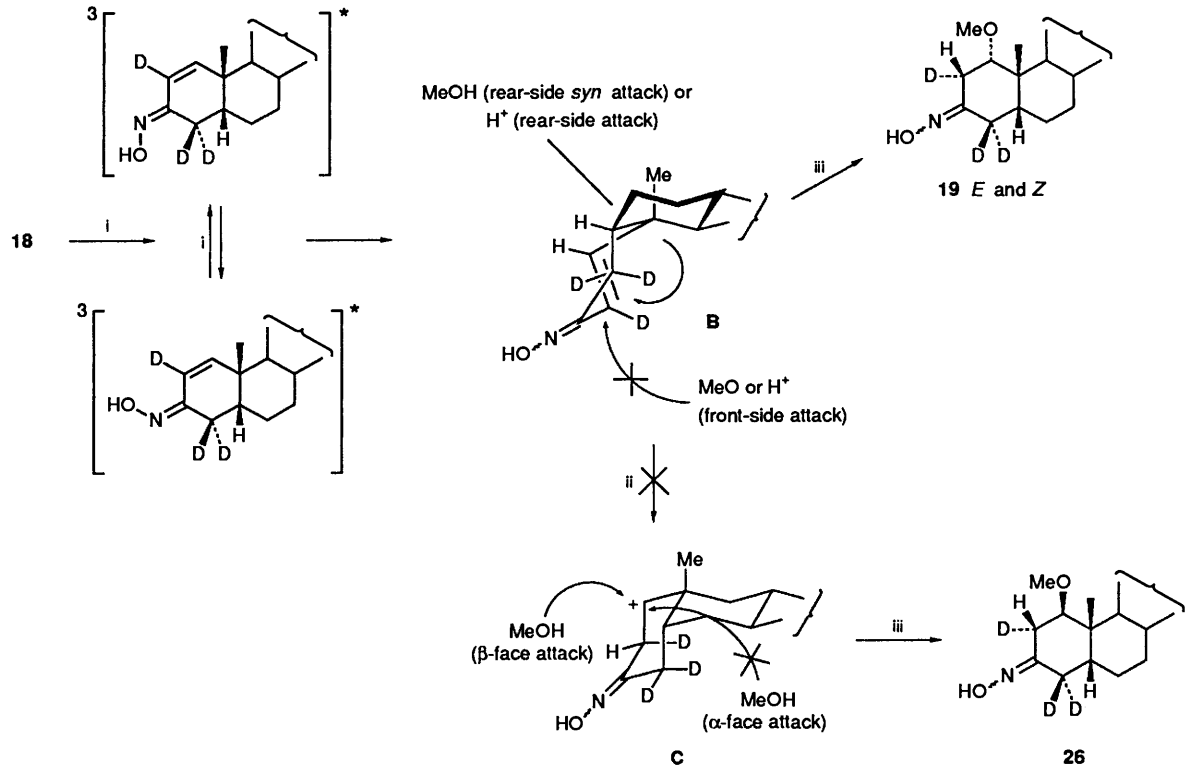
23 **24** *E* and *Z*; $R^1 = R^2 = H$; **25** *E* and *Z*; R^1 = D, R^2 = H

Scheme 3 *Reagents and conditions:* i, *hν*, MeOH; ii, *hν*, MeOD

yield, as well as a new crystalline product **24** in 62.2% yield. High-resolution mass spectrometry as well as spectroscopic results indicated that the product was a 20:23 mixture of (*E*)-(*anti*) and (*Z*)- (*syn*) 1-methylene-5β-cholestan-3-one oximes **24**; the 400 MHz NMR spectrum exhibited three singlets at δ 4.79, 4.87 and 4.92, that are assignable to 1′-H_a of the *E* and *Z* isomers, 1′-H_b of the *E*-isomer, and 1′-H_b of the *Z*-isomer, respectively. All of the assignments of 2α, 2β-, 4α- and 4β-H of both *E* and *Z* isomers are given in the Experimental section.

Deuterium-labelling Experiments on the Photodeconjugation of Oxime **23** (*Scheme* 3).—A deuterium-labelling study of the photodeconjugation of oxime **23** in methan[^{2}H]ol was carried out under the conditions described for the deuterium labelling of the photodeconjugation of 1-methyl-5α-cholest-1-en-3-one oxime **6**.[1] Thus, when a solution of oxime **23** in methan[^{2}H]ol was irradiated under the above mentioned conditions, a 5:4 mixture of the *E* and *Z* isomers **25** of a single, monodeuteriated β,γ-unsaturated ketone oxime was obtained in 59.7% yield. The ^{1}H NMR spectrum exhibited two singlets at δ 2.59 and 2.94. They are assignable to the 2α-H of the *Z*- and *E*-isomer, respectively, since, while the W-couplings (*J* 1.95 Hz) between 2β-H and 4β-H were observed in a pair of signals at δ 2.07 and 3.02, ascribable to 4β-H of the *Z* and *E* isomers **24** (see Experimental section), no W-couplings were observed in the pair of signals at δ 2.07 (dd, *J* 5.03 and 14.4 Hz) and 3.02 (dd, *J* 5.03 and 15.4 Hz) ascribable to, respectively, the 4β-H of the *Z*- and the *E*-isomer in the spectrum of monodeuteriated oximes **25**. These spectral results clearly indicated that the deuterium incorporated at C-2 of oxime **25** occupied the 2β-position. Details concerning analysis of the signals are described in the Experimental section.

Pathways leading to Methanol Adducts **16**, **17**, **19** *and* **20** *in the Photoreactions of Enone Oximes* **14** *and* **18** *in Methanol or in Deuteriomethanol* (*Scheme* 4).—The foregoing results concerning the photolysis of 5β-cholest-1-en-3-one oxime **14** in methanol have shown that while the photolysis of its 5α-isomer **1** in methanol gave isoxazole derivative **2**,[1] no product arising from the analogous rearrangement was formed in the UV excitation of the 5β-isomer. Apart from this difference, the results concerning photolysis are nearly parallel to those obtained in the photolysis of the 5α-isomer;[1] the parent ketone **9** and methanol adducts **16** are formed as the principal adducts, and no lactams arising from the photorearrangement are formed, even though the formation of an accompanying product **15** which arose from a secondary photorearrangement of parent ketone **9** differs from the results obtained in the irradiation of the 5α-isomer.[1] The deuterium-labelling study indicated that the photochemical addition of methanol to the double bond of the oxime **14** is stereospecific, as in the case of the 5α-isomer;[1] the protons and the methoxy group are attached to C-2β and C-1α of adduct **19** in the photolysis of trideuterio oxime **18** in methanol (Scheme 2), while the proton and methoxy group are attached to C-2α and C-1β of adduct **3** in the photolysis of the 5α-isomer.[1] This result shows that the addition of methanol to the double bond of the enone oxime **14** takes place in an entirely parallel manner to that in the case of



Scheme 4 *Reagents and conditions:* i, *hν*; ii, H^+; iii, MeOH

the photochemical addition of methanol to the 5α-oxime. Hence there are two possible paths for the methanol addition to a double bond of the deuteriated oxime **18**, as outlined in Scheme 4: (a) a nucleophilic *syn* addition of methanol from the rear side of the steroidal framework to the photogenerated reactive, twisted double bond of ground-state intermediate **B**; and (b) the addition of methanol to the carbocation **C**, formed by protonation of the double bond from the rear side of the steroidal skeleton, from the less hindered α-face.* The addition of methanol *via* the former route should result in the formation of 1α-methoxy steroid oxime **19**, while the latter should give 1β-methoxy steroid **26**. Thus, the formation of 1α-methoxy steroid oxime **19** in the present experiment indicates that the addition takes place *via* the former route.

Pathway leading to 10β-*Methoxy*-5(10→1)abeo-1β(*H*),-5β,10α(*Me*)-*cholestan*-3-*one* **15**.—10β-Methoxy-5(10→1)*abeo*-1β(H),5β,10α(Me)-cholestan-3-one **15** is a secondary photoproduct formed from a new rearrangement of excited 5β-cholest-1-en-3-one **9** formed from oxime **14** during its irradiation in methanol. The genesis of product **15** has been discussed elsewhere.[10]

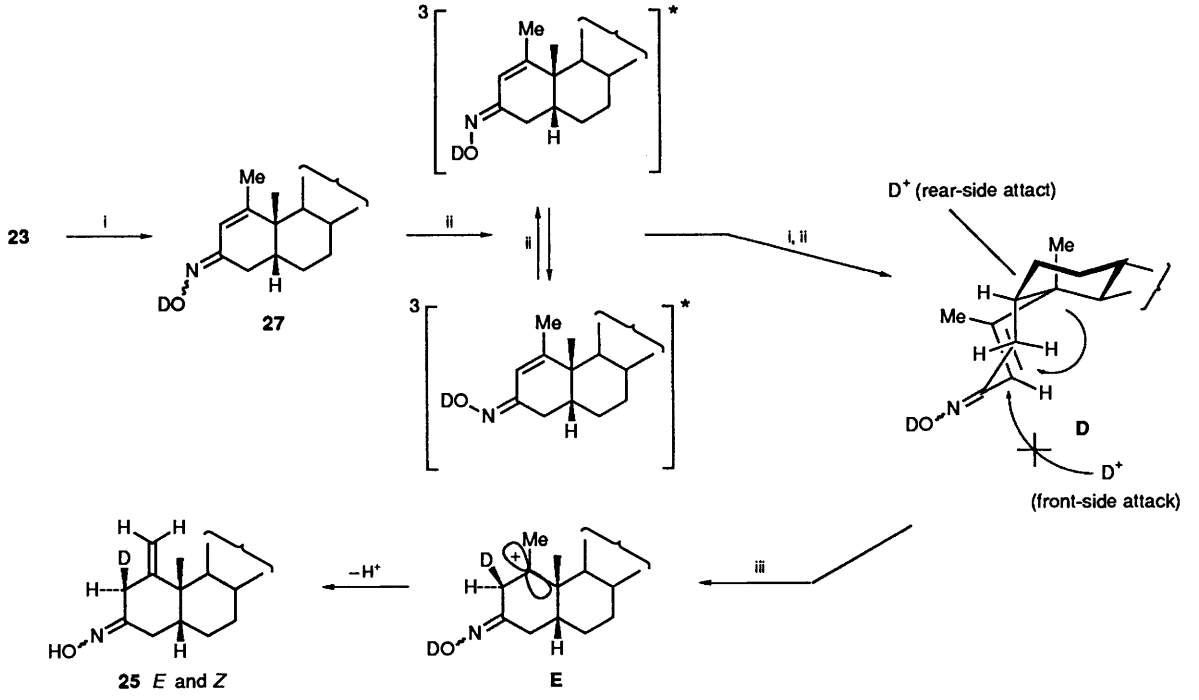
Pathway of the Photodeconjugation of Enone Oximes **23** (*Scheme* 5).—The pathway leading to the β,γ-enone oximes **25** from the excited α,β-enone oxime **23** in methan[^{2}H]ol is outlined in Scheme 5. This pathway is entirely parallel to those leading to the β,γ-enone oximes **8** from the excited 1-methyl-5α-cholest-1-en-3-one oxime **6** in methan[^{2}H]ol as reported in our previous paper.[1] Dissolution of oxime **23** in methan[^{2}H]ol therefore gives its deuterio derivative **27**. Irradiation of the solution generates a twisted ground-state intermediate **D** *via* either singlet- or triplet-excited (*Z*) and (*E*) oximes. The C=C bond of the intermediate is twisted by more than 90°. Stereospecific deuteronation with either a deuteron supplied from the =NOD or the methan[^{2}H]ol then takes place at C-2 of the labile intermediate **D** from the *rear side* of the steroidal framework to give carbocation **E**. The approach of the deuterium from the front side of the steroid is blocked by the C(3)–C(4) and C(4)–C(5) bonds. The deuterium, which is attached β to C-2 instead of α in the case of the photodeconjugation of its 5α-isomer, can be supplied from either the deuterium of the =NOD group in an intra- or intermolecular manner, or from the methan[^{2}H]ol. Although we cannot specify the source of the deuteron, it is likely that the major portion of it comes from a more acidic =NOD group than from MeOD, in an intramolecular manner.

As in the case of 5α-isomer **6**, the loss of a proton from the 1-methyl group takes place from the carbocation **E** generated from excited 1-methyl-5β-enone **23** (Scheme 5) in preference to the fragmentation which leads to the formation of isoxazole derivatives.

The results reported in this and previous papers[1,2,11] have shown that the principal reaction of steroidal 1-en-3-one oximes in methanol upon irradiation was a stereospecific addition of either methanol or a proton to the photogenerated, twisted, ground-state double bond of the oximes from the rear side of the steroid framework. This leads to either methanol adducts or an isoxazole derivative, while the major reaction of the steroidal oximes of 4-en-3-ones and 5-en-7-ones in methanol upon irradiation was a regiospecific rearrangement to the corresponding enamine-type lactams.[11]

The factors which lead to these differences in the photoreaction products in steroidal cyclohexenone oximes are obscure. The difficulties concerning the photogeneration of the twisted, ground-state double bond in the steroidal cyclo-

* The italicized part of the following statement concerns the paths for methanol addition to the 5α-enone oxime discussed in a previous paper:[1] 'The formation of 1β-methoxy steroids indicates that the methanol adducts are formed through the latter path, since the addition by the former route *may lead to more stable* 1α-*methoxy steroids*, **23**, instead of the 1β-methoxy steroid **17**'. It should be replaced by '*takes place from the less hindered* α-*face to give* 1α-*methoxy steroid* **23**.'



Scheme 5 *Reagents and conditions:* i, MeOD; ii, *hν*; iii, D^+

hexenone oximes, such as steroidal 4-en-3-one oximes,[11] in which the double bonds are located at their bridgehead positions, would be one apparent factor in suppressing photoreactions at their α,β-double bond.

The results reported in this and the previous paper [1] have also shown that the major reaction of the 1-methyl derivatives of steroidal 1-en-3-one oximes upon irradiation was photoisomerization to their β,γ-unsaturated isomers, regardless of *cis* or *trans* fusion of their A,B-rings. The photodeconjugation of cyclohexenone oximes has never been reported; these examples therefore represent the first case. The mechanism of this photodeconjugation, which involves the stereospecific addition of a proton to the photogenerated, twisted double bond of the oximes from the rear side of the steroidal framework, followed by the loss of a proton, was firmly established by a deuterium-labelling study.[1]

The photodeconjugation of α,β-unsaturated carboxylic acid esters[12] is well known, and the mechanism involving intramolecular hydrogen abstraction has been established.[13] The photodeconjugation of cycloalkenones has also been recorded for both steroidal[14] and non-steroidal systems.[14,15] The photodeconjugation of $\Delta^{1,9}$-10-methyl-2-octalone, however, has been shown to take place *via* a different pathway.[16,17]

We have found that the photodeconjugation parallel to that of the cyclohexenone oximes (**6** and **23**), described in this and a previous paper,[1] takes place as the major reaction when the parent enones (**10** and **11**) in methanol are irradiated with a low-pressure mercury arc. Our study concerning the mechanism of deconjugation by deuterium labelling, however, has met with some difficulty, due to a ready exchange of the deuterium incorporated at the α-position of the resulting β,γ-enones by protons through their photogenerated enols.

We assume, however, that the present mechanism for the cyclohexenone oximes can be applied to the photodeconjugation of, at least, the parent enones, such as **10** and **11**.

Experimental

Regarding the instruments used and the general procedure, see the previous paper.[1]

2β,4β-*Dibromo*-5β-*cholestan*-3-*one*.—To a solution of 5β-cholestan-3-one[4] (100 mg, 0.26 mmol) in glacial acetic acid (3 cm^3) at 60 °C was added pyridine hydrobromide perbromide (170 mg, 0.53 mmol). The solution was stirred for 30 min at 60 °C, and the solvent was then removed under reduced pressure (rotary evaporator). Saturated aq. sodium carbonate and diethyl ether were added to the residue. After separation of the organic layer, the aqueous solution was extracted with diethyl ether. The combined organic layers were washed successively with water and saturated brine, and were dried over anhydrous magnesium sulfate. Evaporation of the solvent gave a crude dibromo ketone (114 mg),[5] δ 0.69 (3 H, s, 18-H_3), 1.11 (3 H, s, 19-H_3), 4.67 (1 H, dd, *J* 5.5 and 13.3, 2α-H) and 4.97 (1 H, d, *J* 9.4, 4α-H). This bromide was used for dehydrobromination without further purification.

4β-*Bromo*-5β-*cholest*-1-*en*-3-*one*.—Calcium carbonate (200 mg, 2 mmol) was added to a solution of the above mentioned dibromo ketone (114 mg) in DMA (1.2 cm^3). The solution was heated under reflux for 30 min and was then filtered through Celite. The filtrate was worked up as in the case of dehydrobromination of 2α-bromo-1α,4,4-trimethyl-5α-cholestan-3-one.[1] The product was subjected to PLC (benzene) to give two fractions. A more mobile fraction (49 mg, 41%) was the *title* 4β-*bromo enone*, m.p. 105–107 °C (from acetone); ν_{max}/cm^{-1} 1695 (C=O); δ(90 MHz) 0.70 (3 H, s, 18-H_3), 1.27 (3 H, s, 19-H_3), 5.03 (1 H, d, *J* 13.2, 4α-H), 6.01 (1 H, d, *J* 10.1, 2-H) and 6.88 (1 H, d, *J* 13.2, 4α-H), 6.01 (1 H, d, *J* 10.1, 2-H) and 6.88 (1 H, d, *J* 10.1, 1-H); *m/z* 464 (M^+, 5.4), 462 (M^+, 5.5), 383 [$(M - Br)^+$, 39] and 121 (100%). HR-MS (Found: M^+, 462.2489. $C_{27}H_{43}{}^{79}BrO$ requires M, 462.2497. Found: M, 464.2469. $C_{27}H_{43}{}^{81}BrO$ requires M, 464.2477).

The less mobile fraction (18 mg, 18% was cholesta-1,4-dien-3-one.

5β-*Cholest*-1-*en*-3-*one* **9**.[3]—To a solution of 4β-bromo-5β-cholest-1-en-3-one (550 mg, 1.24 mmol) and AIBN (110 mg, 0.67 mmol) in dry benzene (45 cm^3) was added tributyltin hydride (0.46 cm^3, 1.71 mmol). The solution was stirred under nitrogen at 60 °C for 1 h. Evaporation of the solvent gave a

residue. To this were added diethyl ether (2 cm^3) and potassium fluoride (2 g); the solution was then stirred for 1 h. After filtration of the solution, the solvent was removed under reduced pressure to give enone **9** (348 mg, 75%), m.p. 104–105 °C (from methanol–acetone) [lit.,[3g] 93 °C; lit.,[3c] 85–87 °C (from EtOH)]; ν_{max}/cm^{-1} 1683 (C=O), 1270, 849 and 793; δ(90 MHz) 0.69 (3 H, s, 18-H_3), 1.19 (3 H, s, 19-H_3), 5.88 (1 H, d, *J* 10.1, 2-H) and 6.82 (1 H, d, *J* 10.1, 1-H); *m/z* 384 (M^+, 21.7), 271 (11.3), 122 (100) and 109 (36.6%).

5β-*Cholest*-1-*en*-3-*one Oxime* **14**.—Enone **9** (348 mg, 0.93 mmol), hydroxylamine hydrochloride (320 mg, 4.61 mmol) and sodium acetate trihydrate (200 mg, 2.7 mmol) in ethanol (15 cm^3) were stirred for 40 min at room temperature. Evaporation of the solvent left a residue, which was worked up in the usual way. The product was purified by PLC [(8:1) benzene–diethyl ether] to give *enone oxime* **14** (335 mg, 93%), m.p. 130–131 °C (from acetone) (Found: C, 81.0; H, 11.1; N, 3.5%; M^+, 399.3529. $C_{27}H_{45}NO$ requires C, 81.14; H, 11.35; N, 3.51%; M, 399.3501); ν_{max}/cm^{-1} 3206 (OH), 962 and 783; δ(270 MHz) 0.67 (3 H, s, 18-H_3), 1.12 (3 H, s, 19-H_3), 6.01 (1 H, d, *J* 10.3, 2-H) and 6.08 (1 H, d, *J* 10.3, 1-H); *m/z* 399 (M^+, 83.0) 832 [$(M - OH)^+$, 100], 286 (16.8), 137 (35.6), 124 (85.7) and 108 (58.6%); ν_{max}(MeOH)/nm 261 (ε 12 000).

1β-*Methyl*-5β-*cholestan*-3-*one* **12**.—To a solution of copper(I) iodide (850 mg) in diethyl ether (15 cm^3) at 0 °C under nitrogen was added (dropwise) methyllithium (8.0 cm^3; 1.5 mol dm^{-3} solution in diethyl ether). After the solution had been stirred for 30 min a solution of enone **9** (800 mg) in diethyl ether (15 cm^3) was added. The solution was then stirred for 1 h before being treated with saturated aq. ammonium chloride, and the organic layer was separated. The aqueous layer was extracted with diethyl ether. The combined ethereal solution was washed successively with water and brine, and was then dried over anhydrous sodium sulfate. Evaporation of the solvent gave 1β-methyl ketone **12** (825 mg), which was subjected to PLC (dichloromethane) to give pure *ketone* **12** as a glass (802 mg, 96.2%) (Found: M^+, 400.3705. $C_{28}H_{48}O$ requires M, 400.3705); ν_{max}(neat)/cm^{-1} 1718 (C=O); δ(400 MHz) 0.68 (3 H, s, 18-H_3), 0.88 (3 H, d, *J* 6.59, 1β-Me), 1.01 (3 H, s, 19-H_3), 2.01 (1 H, d, *J* 6.10, 4β-H), 2.06 (1 H, d, *J* 6.10, 2β-H), 2.07–2.24 (1 H, m, 1α-H), 2.63 (1 H, d, *J* 6.34, 4α-H) and 2.66 (1 H, d, *J* 6.10, 2α-H); *m/z* 400 (M^+, 65.4), 385 [$(M - Me)^+$, 5.96], 315 (100.0), 245 (29.9), 159 (65.3), 136 (42.0), 107 (54.2), 95 (61.3) and 55 (53.5%).

2β-*Bromo*-1β-*methyl*-5β-*cholestan*-3-*one* **13**.—To a solution of 1β-methyl ketone **12** (50 mg) in glacial acetic acid (2 cm^3) was added pyridine hydrobromide perbromide (96 mg). This solution was stirred for 3 h before ice–water was added. The product, collected by filtration, was dissolved in diethyl ether. The ethereal solution was washed successively with saturated aq. sodium hydrogen carbonate and water; it was then dried over anhydrous sodium sulfate. Evaporation of the solvent gave crude 2,4-dibromo ketone (70 mg).

A solution of the dibromo ketone (70 mg) in a mixture of glacial acetic acid (1.3 cm^3) and chloroform (0.52 cm^3) was flushed with nitrogen. To this solution at 0 °C was added chromium(II) acetate (21.3 mg); the solution was stirred for 11 h at 0 °C during the addition of chromium(II) acetate (21.3 mg) 11 times, once every hour. The solution was then neutralized by addition of saturated aq. sodium hydrogen carbonate, and then was extracted with diethyl ether. The extract was washed successively with water and brine, and was then dried over anhydrous sodium sulfate. Evaporation of the solvent gave a mixture of products (56 mg), which was subjected to column chromatography to give 2β-*bromo*-1β-*methyl*-5β-*cholestan*-3-*one* **13** (32.5 mg, 81.0% based on consumed ketone **12**), m.p. 150.0–151.0 °C (from ethanol) (Found: C, 70.1; H, 9.9; Br, 16.7. $C_{28}H_{47}BrO$ requires C, 69.89; H, 9.86; Br, 16.59%); and the starting ketone **12** (16.5 mg). ν_{max}/cm^{-1} 1721 (C=O); δ(400 MHz) 0.69 (3 H, s, 18-H_3), 0.98 (3 H, d, *J* 6.84, 1βMe), 1.08 (3 H, s, 19-H_3), 2.31 (1 H, dd, *J* 5.37 and 14.7, 4β-H), 2.53 (1 H, dq, *J* 4.39 and 7.09, 1α-H), 2.74 (1 H, dd, *J* 13.6 and 13.9, 4α-H) and 5.13 (1 H, d, *J* 4.39, 2α-H); *m/z* 480 (M^+, 2.0), 478 (M^+, 2.0), 399 [$(M - Br)^+$, 100.0], 315 (64.4), 245 (11.1), 175 (20.1), 135 (20.8), 107 (27.8), 95 (30.2), 81 (28.5) and 55 (23.8%).

1-*Methyl*-5β-*cholest*-1-*en*-3-*one* **10**.—To a solution of 2β-bromo ketone **13** (570 mg) in *N*,*N*-dimethylformamide (10 cm^3) was added calcium carbonate (595 mg). The solution was heated under reflux for 3 h. After the solution had been filtered through Celite, diethyl ether was added. The ethereal solution was worked up in the usual way. The obtained products (498 mg) were subjected to PLC (dichloromethane) to give two fractions. The more mobile fraction (201 mg) was the starting bromo ketone **13**. The less mobile fraction (260 mg) was 1-*methyl enone* **10**, m.p. 139.0–140.0 °C (from ethanol) (Found: C, 84.2; H, 11.5. $C_{28}H_{46}O$ requires C, 84.35; H, 11.63%); ν_{max}/cm^{-1} 1663 and 1611 (C=CCO); δ(400 MHz) 0.67 (3 H, s, 18-H_3), 1.23 (3 H, s, 19-H_3), 2.00 (3 H, d, *J* 1.46, 1-Me), 2.15 (1 H, dd, *J* 5.37 and 17.8, 4β-H), 2.82 (1 H, dd, *J* 13.7 and 17.8, 4α-H) and 5.87 (1 H, s, 2-H); *m/z* 398 (M^+, 26.4), 356 [$(M - CH_2CO)^+$, 0.77], 285 (9.6), 149 (10.1), 136 (100.0), 95 (16.2) and 55 (16.6%); ν_{max}(MeOH)/nm 245 (ε 12 000).

1-*Methyl*-5β-*cholest*-1-*en*-3-*one Oxime* **23**.—A solution of 1-methyl-5β-cholest-1-en-3-one **10** (180 mg), hydroxylamine hydrochloride (206 mg) and sodium acetate trihydrate (206 mg) in ethanol (13 cm^3) was stirred for 3 h at room temperature. After removal of the solvent, the residue was extracted with water and diethyl ether. The ethereal solution was then worked up in the usual way to give a 20:3 mixture of (*E*)- and (*Z*)-oxime **23** (189 mg). The oxime was recrystallized from a mixture of methanol and acetone to give a 5:1 mixture of the (*E*)- and (*Z*)-oxime (167 mg, 89.6%), m.p. 98–100 °C; ν_{max}/cm^{-1} 3186 (OH), 1632 (C=N) and 977; δ(400 MHz) 0.66 (3 H, s, 18-H_3 of *E*- and *Z*-isomer), 1.16 (3 H, s, 19-H_3 of *E*- and *Z*-isomer), 1.89 (3 H, d, *J* 0.97, 1-Me of *E*-isomer), 1.95 (3 H, br s, 1-Me of *Z*-isomer), 2.64 (1 H, dd, *J* 18.6 and 22.7, 4β-H of *E*-isomer), 2.66 (1 H, br s, 4α-H of *E*-isomer), 5.93 (1 H, d, *J* 0.97, 2-H of *E*-isomer) and 6.65 (1 H, br s, 2-H of *Z*-isomer); *m/z* 413 (M^+, 87.4), 396 [$(M - OH)^+$, 57.3], 382 [$(M - NOH)^+$, 4.7], 315 (8.4), 282 (3.2), 247 (6.9), 151 (28.9) and 138 (100.0%); ν_{max}(MeOH)/nm 243.5 (ε 19 800).

2,4,4-*Trideuterio*-5β-*cholest*-1-*en*-3-*one* **11**.—To a solution of 5β-cholest-1-en-3-one **9** (340 mg) in a mixture of diethyl ether (3.9 cm^3) and methan[^{2}H]ol (10.0 cm^3) was added sodium metal (38.5 mg) under nitrogen. The solution was heated under reflux for 2 days under nitrogen. After addition of glacial acetic acid (0.2 cm^3) the solution was extracted with diethyl ether. The extract was worked up in the usual way. Evaporation of the solvent gave *deuterio enone* **11** (320 mg), m.p. 106–108 °C (from ethanol) (Found: M^+, 387.3557. $C_{27}H_{41}D_3O$ requires M, 387.3581); ν_{max}/cm^{-1} 1675 and 1615 (C=CC=O); δ(400 MHz) 0.69 (3 H, s, 18-H_3), 1.19 (3 H, s, 19-H_3) and 6.83 (1 H, s, 1-H); *m/z* 387 (M^+, 49.3), 372 (3.9), 274 (20.9), 136 (35.7), 125 (100.0), 112 (64.0) and 81 (36.9%).

(E)-2,4,4-*Trideuterio*-5β-*cholest*-1-*en*-3-*one Oxime* **18**.—2,4,4-Trideuterio enone **11** (300 mg), hydroxylamine hydrochloride (380 mg), sodium acetate trihydrate (380 mg) and ethanol (24 cm^3) were stirred together for 3 h at room temperature. Evaporation of the solvent gave a residue, which was extracted with diethyl ether. The ethereal solution was worked up in the usual way to give crude oxime **18** (312 mg). Pure (E)-*oxime* (291 mg), m.p. 139–140 °C, was obtained by recrystallization from methanol–acetone (Found: M^+, 402.3688. $C_{27}H_{42}D_3NO$

requires M, 402.3691); ν_{max}/cm^{-1} 3584 (OH), 1626 (C=C), 1258, 1160 and 1007; δ(400 MHz) 0.67 (3 H, s, 18-H$_3$), 1.12 (3 H, s, 19-H$_3$) and 6.09 (1 H, s, 1-H); *m/z* 402 (M$^+$, 63.4), 385 [(M − OH)$^+$, 100.0], 127 (50.8), 109 (29.2), 95 (30.0), 81 (29.3) and 55 (32.6%).

The Photoreaction of 5β-*Cholest*-1-*en*-3-*one Oxime* **14**. (a) *In methanol.*—A solution of enone oxime **14** (300 mg) in methanol (198 cm^3) in a quartz tube was flushed with nitrogen. The solution was irradiated with a low-pressure mercury arc, generated from a Rayonet photochemical reactor, for 15 h under nitrogen. Evaporation of the solvent under reduced pressure gave a product mixture which was subjected to PLC [(8:1) benzene–diethyl ether] to give five fractions A, B, C, D and E in order of their mobility on PLC. The most mobile fraction A (21 mg, 7%) was 1α-*methoxy*-5β-*cholestan*-3-*one* **17** as a glass (Found: M$^+$, 416.3664. $C_{28}H_{48}O_2$ requires M, 416.3654); ν_{max}(neat)/cm^{-1} 1721 (C=O) and 1095; δ(400 MHz) 0.67 (3 H, s, 18-H$_3$), 1.15 (3 H, s, 19-H$_3$), 2.01 (1 H, ddd, *J* 1.96, 4.64 and 18.3, 4β-H), 2.47 (1 H, dd, *J* 11.48 and 14.6, 2α-H), 2.65 (1 H, ddd, *J* 1.96, 3.42 and 14.6, 2β-H), 2.68 (1 H, dd, *J* 13.7 and 18.3, 4α-H), 2.97 (1 H, dd, *J* 3.9 and 11.48, 1β-H) and 3.27 (3 H, s, 1α-OMe); *m/z* 416 (M$^+$, 16.9), 401 [(M − Me)$^+$, 4.5], 384 [(M − OMe)$^+$, 14.5], 369 (5.9), 314 (30.0), 229 (17.1), 161 (30.2), 107 (42.1), 100 (100.0) and 81 (59.0%).

Fraction **B** (83 mg, 30.6% based on converted oximes) was identical with the parent enone **9**.

Fraction C (19 mg, 6%) was a 39:10 mixture of *E* and *Z* oximes.

Fraction D (19 mg, 6%) was *rearranged ketone* **15**, m.p. 140–142 °C (from ethanol) (Found: C, 80.2; H, 11.9. $C_{28}H_{48}O_2$ requires C, 80.61; H, 11.61%); ν_{max}/cm^{-1} 1734 (C=O) and 1068; δ(400 MHz) 0.66 (3 H, s, 18-H$_3$), 1.08 (3 H, s), 2.1–2.24 (1 H, m), 2.27–2.38 (2 H, m) and 2.48–2.58 (2 H, m); *m/z* 416 (M$^+$, 8.70, 401 [(M − Me)$^+$, 2.5], 384 [(M − OMe)$^+$, 2.1], 247 (44.2), 139 (100.0), 111 (40.9), 85 (59.0) and 55 (36.3%).

Fraction E (38 mg, 12%) was a 1:1 mixture of E and Z (1α-*methoxy*-5β-*cholestan*-3-*one oximes* **16**, m.p. 69–71 °C (from methanol–acetone) (Found: M$^+$, 431.3781. $C_{28}H_{49}NO_2$ requires M, 431.3763); ν_{max}/cm^{-1} 3216 (OH), 1665, 1254, 859, 806 and 760; δ(400 MHz) 0.66 (3 H, s, 18-H$_3$), 1.12 (3 H, s, 19-H$_3$), 1.94 (1 H, dd, *J* 3.42 and 12.2, 4β-H of *Z*-isomer), 1.95 (1 H, dd, *J* 3.42 and 12.2, 4β-H of *E*-isomer), 2.20 (1 H, *J* 11.72 and 13.2, 4α-H of *Z*-isomer), 2.23 (1 H, *J* 7.8 and 13.7, 2α-H of *E*-isomer), 2.56 (1 H, br t, *J* 14.7, 4α-H of *E*-isomer), 2.60 (1 H, dd, *J* 3.42 and 14.0, 2β-H of *E*-isomer), 2.77 (1 H, dd, *J* 3.90 and 12.2, 1β-H of *Z*-isomer), 2.84 (1 H, dd, *J* 3.90 and 12.0, 1β-H of *E*-isomer), 2.85 (1 H, dd, *J* 3.90 and 16.1, 2α-H of *Z*-isomer), 3.30 (3 H, s, 1α-OMe of *E*-isomer), 3.33 (3 H, s, 1α-OMe of *Z*-isomer) and 3.50 (1 H, dd, *J* 3.42 and 14.2, 2β-H of *Z*-isomer); *m/z* 431 (M$^+$, 26.8), 399 [(M − OMe)$^+$, 28.1], 382 (30.6), 124 (70.9), 115 (100.0), 95 (43.2), 81 (48.1) and 55 (78.1%).

Photoreaction of 2,4,4-*Trideuterio*-5β-*cholest*-1-*en*-3-*one Oxime* **18**.—A solution of oxime **18** (240 mg) in methanol 158 cm^3) was irradiated for 16 h as in the photolysis of oxime **14**. After evaporation of the solvent, the product was subjected to PLC [(8:1) benzene–diethyl ether] to give five fractions (A–E) in the order of mobility on the TLC plate. Fraction A (15 mg, 6%) was 2α,4,4-*trideuterio*-1α-*methoxy*-5β-*cholestan*-3-*one* **20**, obtained as a glass (Found: M$^+$, 419.3831. $C_{28}H_{45}D_3O_2$ requires M, 419.3843); ν_{max}(neat)/cm^{-1} 1721 (C=O) and 1095; δ(400 MHz) 0.675 (3 H, s, 18-H$_3$), 1.160 (3 H, s, 19-H$_3$), 2.624 (1 H, d, *J* 3.42, 2β-H), 2.962 (1 H, d, *J* 3.42, 1β-H) and 3.272 (3 H, s, 1α-OMe); *m/z* 419 (M$^+$, 50.5), 404 [(M − Me)$^+$, 11.7], 387 [(M − OMe)$^+$, 38.3], 372 (14.0), 332 (14.7), 314 (100.0), 274 (18.1), 232 (38.7), 161 (63.9), 121 (45.8), 103 (90.6) and 81 (86.5%).

Fraction B (49 mg, 24.0%) was 2,4,4-trideuterio-5β-cholest-1-en-3-one **11**.

Fraction C (29 mg, 12.0%) was starting oxime **18**.

Fraction D (10 mg, 3.8%) was *rearranged ketone* **21**, m.p. 141–142 °C (from ethanol) (Found: M$^+$, 419.3828. $C_{27}H_{45}D_3O_2$ requires *M*, 419.3843); ν_{max}/cm^{-1} 1743 (C=O), 1069 and 947; δ(400 MHz) 0.697 (3 H, s, 18-H$_3$), 1.083 (3 H, s, 10α-Me), 2.1–2.2 (1 H, m), 2.26–2.38 (2 H, m), 2.48–2.58 (2 H, m) and 3.090 (3 H, s, OMe); *m/z* 419 (M$^+$, 13.2), 402 [(M − Me)$^+$, 35.7], 385 [(M − OMe)$^+$, 53.9], 247 (75.5), 142 (100.0), 114 (35.0), 86 (50.6) and 55 (67.8%).

Fraction E was a 5:7 mixture of E and Z *oximes* **19** (19 mg, 7.3%), m.p. 68–72 °C (from methanol–acetone) (Found: M$^+$, 434.3970. $C_{28}H_{46}D_3NO_2$ requires *M*, 343.3951); ν_{max}/cm^{-1} 3084 (OH), 1717, 1659 and 1275; δ(400 MHz) 0.656 (3 H, s, 18-H$_3$), 1.115 (3 H, s, 19-H$_3$), 2.578 (1 H, d, *J* 3.9, 2β-H of *Z*-isomer), 2.763 (1 H, d, *J* 3.9, 1β-H of *E*-isomer), 2.826 (1 H, d, *J* 3.9, 1β-H of *Z*-isomer), 3.293 (3 H, s, 1α-OMe of *Z*-isomer), 3.327 (3 H, s, 1α-OMe of *E*-isomer) and 3.482 (1 H, d, *J* 3.9, 2β-H of *E*-isomer); *m/z* 434 (M$^+$, 48.6), 417 [(M − OH)$^+$, 49.0], 402 [(M − OMe)$^+$, 85.9], 385 [(M − OMe − OH)$^+$ 56.0], 126 (76.8), 118 (100.0), 95 (59.5), 81 (62.0) and 59 (99.3%).

Photoreaction of (E)- *and* (Z)-1-*Methyl*-5β-*cholest*-1-*en*-3-*one Oximes* **23** (a) *In methanol.*—A solution of enone oximes **23** (50 mg) in methanol (32 cm^3) in a quartz tube was flushed with nitrogen. The solution was then irradiated with a low-pressure mercury arc (Rayonet photochemical reactor) for 5 h under nitrogen. Evaporation of the solvent under reduced pressure gave a product mixture, which was subjected to PLC [(4:1) benzene–diethyl ether] to give two products, A and B. The more mobile product (10.6 mg, 21.9%) was 1-methyl-5β-cholest-1-en-3-one **10**.

The less mobile product (31.1 mg, 62.2%), m.p. 122–123 °C (from acetone–methanol), was a 20:23 *mixture* of Z and E *isomers* of *oximes* **24** (Found: M$^+$, 413.3678. $C_{28}H_{47}NO$ requires *M*, 413.3699); ν_{max}/cm^{-1} 3198 (OH), 1637 and 898; δ(400 MHz) 0.657 (3 H, s, 18-H$_3$), 1.181 (3 H, s, 19-H$_3$), 2.071 (1 H, ddd, *J* 1.95, 5.13 and 14.9, 4β-H of *Z*-isomer), 2.304 (1 H, t, *J* 14.2, 4α-H of *Z*-isomer), 2.600 (1 H, t, *J* 15.1, 2α-H of *E*-isomer), 2.685 (1 H, t, *J* 14.2, 4α-H of *E*-isomer), 2.836 (1 H, dd, *J* 1.95 and 14.9, 2β-H of *E*-isomer), 2.962 (1 H, d, *J* 15.1, 2α-H of *Z*-isomer), 3.020 (1 H, ddd, *J* 1.95, 5.13 and 15.6, 4β-H of *E*-isomer), 3.857 (1 H, dd, *J* 1.95 and 14.7, 2β-H of *Z*-isomer), 4.790 (2 H, s, 1′-H^a of *E*- and *Z*-isomers), 4.866 (1 H, s, 1′-H^b of *E*-isomer) and 4.920 (1 H, s, 1′-H^b of *Z*-isomer); *m/z* 413 (M$^+$, 78.8), 397 [(M − OH)$^+$, 62.3], 383 [(M − NOH)$^+$, 5.11], 300 (8.9), 247 (19.6), 160 (14.8), 151 (48.1), 138 (87.6) and 122 (100.0%).

(b) *In methan*[^{2}H]*ol.* A solution of enone oximes **23** (50 mg) in methan[^{2}H]ol (32 cm^3) in a quartz tube was flushed with nitrogen. The solution was irradiated for 8 h under the conditions described above. Removal of the solvent and separation of the product mixture by PLC gave 1-methyl-5β-cholest-1-en-3-one **10** (10.5 mg, 21.8%) and deuterio-β,γ-enone oximes **25** (29.9 mg, 59.7%), m.p. 120–123 °C (from acetone–methanol). The *oximes* **25** were a 4:5 mixture of *Z* and *E* isomers (^{1}H NMR) (Found: M$^+$, 414.3700. $C_{28}H_{46}DNO$ requires *M*, 414.3720); ν_{max}/cm^{-1} 3196 (OH), 1640 and 898; δ(400 MHz) 0.657 (3 H, s, 18-H$_3$), 1.179 (3 H, s, 19-H$_3$), 2.071 (1 H, dd, *J* 5.03 and 14.4, 4β-H of *Z*-isomer), 2.587 (1 H, s, 2α-H of *Z*-isomer), 2.941 (1 H, s, 2α-H of *E*-isomer), 3.022 (1 H, dd, *J* 5.03 and 15.4, 4β-H of *E*-isomer), 4.787 (1 H, s, 1′-H^a of *E* and *Z* isomers), 4.859 (1 H, s, 1′-H^b of *E*-isomer) and 4.917 (1 H, s, 1′-H^b of *Z*-isomer); *m/z* 414 (M$^+$, 98.1), 397 [(M − OH)$^+$, 81.3], 381 [(M − NOH)$^+$, 5.8], 315 (10.5), 247 (15.7), 152 (54.1), 139 (100.0) and 123 (64.3%).

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