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# Photorearrangements of Some Methyl-substituted Cholest-5-en-3β-ol Nitrites[1)]

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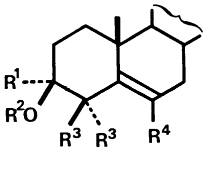
Photolysis of 6-methylcholest-5-en-3β-ol nitrite and 4,4,6-trimethylcholest-5-en-3β-ol nitrite in benzene with monochromatic light respectively gave a seven-membered cyclic hydroxamic acid arising from rearrangement albeit in low yields. Photolysis of 3α-methylcholest-5-en-3β-ol nitrite and 3α,4,4-trimethylcholest-5-en-3β-ol nitrite respectively gave a nitroso dimer arising from β-scission.

In a series of previous papers,[2)] we have reported the results of the photorearrangements of several steroidal and nonsteroidal cyclic homoallyl alcohol nitrites.[2)]

These studies have shown that the products in the photorearrangement of cyclic homoallyl alcohol nitrites are always those arising from the combination of nitrogen monooxide and the less substituted carbon terminus of the allyl radical intermediates. These are generated by the β-scission of the corresponding oxyl radicals, with the formation of more highly substituted olefins.

We have found, however, an exception to this rule in the photorearrangement of 4,4-dimethylcholesteryl nitrite[2)] in which the nitrogen monooxide shifts regioselectively to the more substituted terminus of the intermediary allyl radical. This reverse regioselectivity observed in the radical combination between the allyl radical and nitrogen monooxide was explained as due to the shielding of the C-6 by the 10β-methyl group and the *quasi*-axial 7α-H.[3)]

In order to gain more insight into the effects of alkyl substitution around the reacting radical center, we investigated the photoreactions of two 6-methylcholest-5-en-3β-ol nitrites (**2**) and (**4**) and two 3α-methylcholest-5-en-3β-ol nitrites (**6**) and (**8**) with monochromatic light as well as with Pyrex-filtered light. The photolysis of these nitrites with monochromatic light was especially desirable in order to avoid the secondary photo-decomposition of the photo-products.



(1) $R^1=R^2=R^3=H$, $R^4=CH_3$
(2) $R^1=R^3=H$, $R^2=NO$, $R^4=CH_3$
(3) $R^1=R^2=H$, $R^3=R^4=CH_3$
(4) $R^1=H$, $R^2=NO$, $R^3=R^4=CH_3$
(5) $R^1=CH_3$, $R^2=R^3=R^4=H$
(6) $R^1=CH_3$, $R^2=NO$, $R^3=R^4=H$
(7) $R^1=R^3=CH_3$, $R^2=R^4=H$
(8) $R^1=R^3=CH_3$, $R^2=NO$, $R^4=H$

6-Methylcholest-5-en-3β-ol nitrite (**2**), 4,4,6-trimethylcholest-5-en-3β-ol nitrite (**4**) and 3α-methylcholest-5-en-3β-ol nitrite (**6**) were prepared from the corresponding 3β-ols (**1**),[4,5)] (**3**),[5)] and (**5**),[6)] by the standard method. Nitrosation of 3α,4,4-trimethylcholest-5-en-3β-ol (**7**)[7)] with nitrosyl chloride–pyridine by the standard method, was found to be difficult and to give a 1:2.4 mixture of the starting alcohol and nitrite **8** as determined by the signal ratio of 6-H in the $^1H$ NMR spectrum.

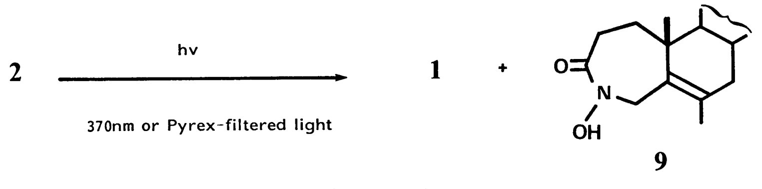
Irradiation of nitrite **2** in dry benzene with 370 nm monochromatic light gave mainly the parent alcohol (**1**) (57%) arising from a hydrogen abstraction of the corresponding oxy radical together with a 7% yield of a crystalline product (**9**). This was proved to be 4-hydroxy-6-methyl-4-aza-*A*-homocholest-5-en-3-one, a hydroxamic acid, from its spectroscopic data (Scheme 1).

Photolysis of nitrite **2** with a Pyrex-filtered light gave **9** in a much higher yield (37%) and the parent alcohol **1** (26%).

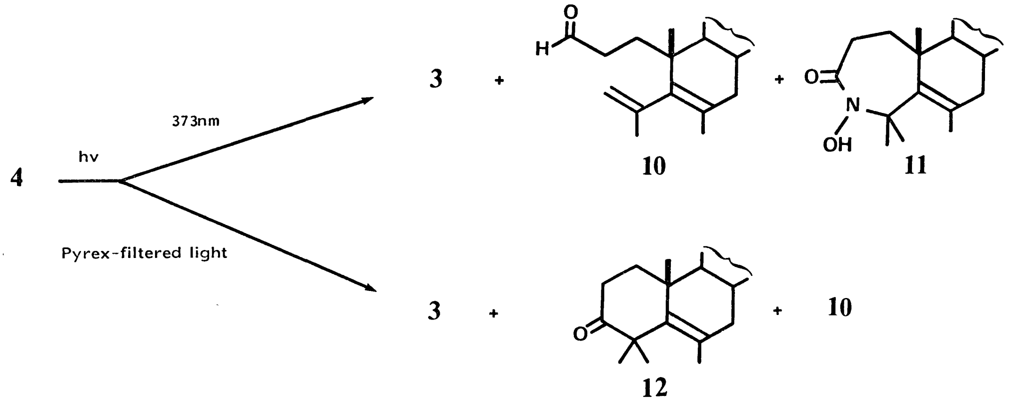
Photolysis of nitrite **4** with a 373 nm light also gave a mixture of products from which the parent alcohol **3** (18%), 4,6-dimethyl-4-methylene-3,4-secocholest-5-en-3-al (**10**) (25%) and 4-hydroxy-4a,4a,6-trimethyl-4-aza-*A*-homocholest-5-en-3-one (**11**) (13%) were obtained by preparative TLC (Scheme 2).

Photolysis of **4** with a Pyrex-filtered light was also found to give the parent alcohol **3** (18%) and a secoaldehyde **10** (6%) together with 4,4,6-trimethylcholest-5-en-3-one (**12**)[8)] (4%). No hydroxamic acid **11**, however, was found in the product mixture.

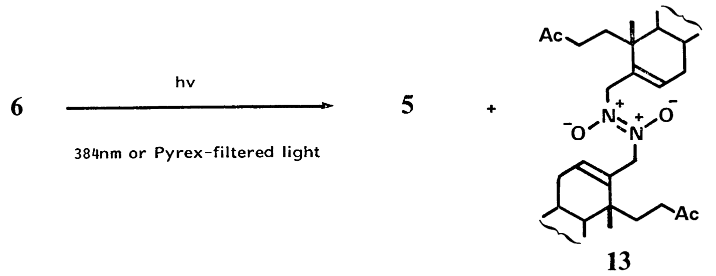
Although the observed differences between the results of the photolysis with monochromatic light and those with a Pyrex-filtered light are not clear at present, it has thus again been shown that seven-membered cyclic hydroxamic acid can be prepared from the photoreaction of 3-hydroxy-$\Delta^5$-steroid nitrites.[2)] It should be noted that the product of the photorearrangement of (**2**) is a hydroxamic acid **9** and not the corresponding seven-membered cyclic nitrone.[9)] This



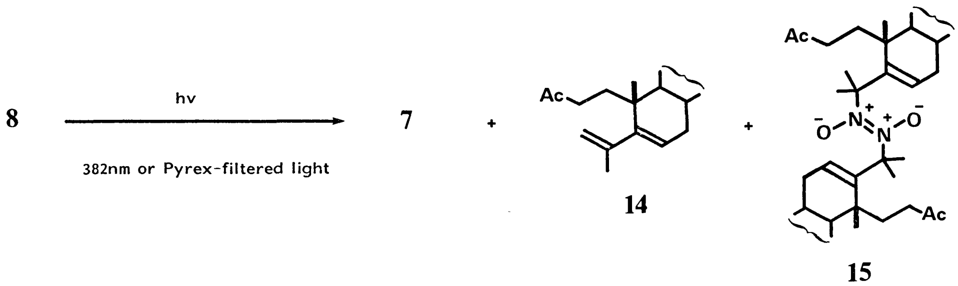
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

result is entirely parallel with that obtained in the photorearrangement of cholesterol nitrite.[2] The reason why the nitrone is not formed in this photorearrangement of cyclic homoallyl alcohol nitrite has already been discussed in the previous paper.[2]

We then studied the photolysis of two 3α-methylcholest-5-en-3β-ol nitrites (**6**) and (**8**) from which hydroxamic acids can not be formed even after β-scission.

The photolysis of 3α-methylcholest-5-en-3β-ol nitrite (**6**) with a 384 nm light resulted in the formation of a mixture of the products. Preparative TLC of the product gave the parent alcohol **5** (14%) and a crystalline nitroso dimer (**13**) (12%) together with several ill-defined products. The structure of the nitroso dimer **13** as (*E*)-4,4′-azobis(3,4-seco-3-methylcholest-5-en-3-one) *N*,*N*′-dioxide was confirmed by means of spectroscopy (see Experimental section). The photolysis of **6** with a Pyrex-filtered light gave a similar result with a better yield of the nitroso dimer (21%) (Scheme 3).

On the other hand, irradiation of a mixture of the alcohol **7** and the nitrite **8** with 382 nm monochromatic light gave three products; an amorphous seco-ketone (**14**)(13%), the parent alcohol **7** (23%) and an unstable amorphous nitroso dimer(**15**) (11%). The structures of **14** and **15** were shown to be 3,4-dimethyl-4-methylene-3,4-secocholest-5-en-3-one and (*E*)-4,4′-azobis (3,4-seco-3,4,4-trimethylcholest-5-en-3-one) *N*,*N*′-dioxide on the basis of their $^1$H NMR, UV, IR, and Mass spectra (Scheme 4).

The photolysis of **8** with a Pyrex-filtered light also gave the seco-ketone **14** and the nitroso dimer **15** in better yields together with a lower yield of the parent 3β-ol **7**.

It has thus again been shown that the nitrogen monooxide migrates to the more substituted carbon terminus of the intermediary allyl radical in the photolysis of 4,4-dimethyl-3β-hydroxy-Δ$^5$-steroid nitrite. As has been discussed in the previous paper,[2] this anomaly in the site of the combination of radicals may be steric in its origin and may be due to the fact that the C-6 terminus of the intermediary allyl radical is more shielded for the approach of nitrogen monooxide.

## Experimental

Mp's were determined with a Yanagimoto micro mp apparatus. IR spectra were determined for Nujol mulls, unless stated otherwise, with a JASCO IR-E spectrophotometer. UV spectra were determined with a Hitachi 124 double-beam spectrophotometer, unless stated otherwise. $^1$H NMR spectra were determined with a JEOL PS 100 high-resolution spectrometer (100 MHz) (solvent $CDCl_3$, $SiMe_4$ as internal reference). $^1$H NMR spectra of **8**, **11** and **15** were determined with a JEOL PS 200 high-resolution FT NMR spectrometer (200 MHz). $^{13}$C NMR spectra were determined with a JNM-FX-100 (25 MHz) high-resolution spectrometer ($CDCl_3$, $SiMe_4$ as an internal reference). TLC was carried out on Wako silica gel B-5. Low resolution mass spectra of **9**, **10**, **13**, and **14** were recorded with JEOL JMS-D-300 spectrometer (70 eV) (The Faculty of Agriculture of this University.) Low resolution mass spectra of **11** and **15** were recorded with a JEOL JMS-D-300 spectrometer (70 eV) (The Faculty of Pharmaceutical Sciences of this University). The high resolution mass spectrum of **9** was determined with a JEOL JMS-D-300 spectrometer (70 eV). High resolution mass spectra of **13** and **14** were determined with a JEOL JMS-D 300 spectrometer (70 eV) (The Faculty of Agriculture) and that of **11** was determined with JEOL JMS-D-300 spectrometer (the Faculty of Pharmaceutical Sciences).

*The Procedure of the Photolysis.* *(a) With a Pyrex-filtered Light*: A benzene solution of each nitrite in a Pyrex tube was flushed with oxygen-free nitrogen and irradiated with a 100-W high pressure Hg arc (EIKOSHA PIH-100) until all the nitrite was decomposed. The progress of the photolysis was monitored by TLC at appropriate time intervals.

*(b) With Monochromatic Light*: A solution of each nitrite (2—300 mg) in dry benzene (2—3 cm$^3$) in a quartz cell (10×10×45 mm$^3$) was placed in a chamber of a JASCO CRM-FA grating spectro-irradiator equipped with 2KW Xe arc lamp and irradiated with appropriate monochromatic light until all the nitrite was decomposed. The progress of the photolysis was monitored by TLC.

*Preparation of 6-Methylcholest-5-en-3$\beta$-ol Nitrite (**2**).* To 6-methylcholesterol (800 mg) in pyridine (15 cm$^3$) cooled with Dry Ice–ethanol was added nitrosyl chloride in pyridine dropwise. The solution was stirred for 1 h and poured into water. The crystals (684 mg) of **2** were collected, washed with water and dried. Mp 88.5—90 °C; $[\alpha]^{25}_{D}$ −26.5° (*c* 1.0, $CHCl_3$); IR, 1645 and 1598 (*trans* and *cis* N–O), 782 (O–N), and 680 cm$^{-1}$ (O–N=O); $^1$H NMR, $\delta=0.69$ (3H, s, 18-H), 1.03 (3H, s, 19-H), 1.64 (3H, s, 6-methyl), and 5.19 (1H, broad s, 3$\alpha$-H); UV (benzene) 398 ($\varepsilon$ 45), 374 (94), 362 (75), 348 (60), and 337 (45).

*Photolysis of **2** with Pyrex-filtered Light.* The nitrite (**2**) (620 mg) in benzene (40 cm$^3$) was irradiated for 3 h 20 min. The solvent was evaporated and the product (669 mg) was subjected to preparative TLC with hexane–ethyl acetate (5:1) to give eight fractions (A—H) in the order of decreasing mobilities. The fractions A (25 mg), B (33 mg), C (63 mg), E (30 mg), F (29 mg), and H (45 mg) could not be identified. The fraction D (150 mg, 26%) was the parent 3$\beta$-ol. The fraction G (231 mg, 37%) was 4-hydroxy-6-methyl-4-aza-*A*-homo-5-cholesten-3-one (**9**). This hydroxamic acid was recrystallized once from methanol and then from acetone to yield a specimen (179 mg) for analysis. Mp 180—184 °C; $[\alpha]^{20}_{D}$ −8.2° (*c* 1.6 $CHCl_3$); (Found: *m/z* 429.3632. Calcd for $C_{28}H_{47}NO_2$; M 429.3604. Found: C, 78.08; H, 11.06; N, 3.47%. Calcd for $C_{28}H_{47}NO_2$: C, 78.27; H, 11.03; N, 3.26%) IR, 3100 (OH), 1621 (amide C=O), 1230, and 768 cm$^{-1}$; $^1$H NMR ($CDCl_3$), $\delta=0.69$ (3H, s, 18-H), 0.98 (3H, s, 19-H), 1.74 (3H, s, 6-methyl), and 4.27 and 4.32 (2H, AB q, $J=15$ Hz, 4a-$H_2$); $^{13}$C NMR, ($CDCl_3$), $\delta=167.9$ (NCO), 136.1 (C-5) and 129.9 (C-6); MS *m/e* (rel intensity) 429 (M$^+$, 100), 413 (M$^+$−O, 16.8), 412 (M$^+$−OH, 52,3), 384 (57.7), 137 (67.4), 133 (45.7), 95 (28.0), 57 (32.0), 55 (36.9), and 43 (45.5).

*Photolysis of **2** with 370 nm Monochromatic Light.* A solution of 6-methylcholest-5-en-3$\beta$-ol nitrite (**2**) (260 mg) in dry benzene (2.5 cm$^3$) in a quartz cell was placed in a chamber of a JASCO CRM FA grating spectro-irradiator and was irradiated with 370 nm light for 9 h; complete decomposition of the nitrite had occurred after this period. The solvent was removed by distillation under vacuum and the photolysate was subjected to preparative TLC with hexane–ethyl acetate (5:1) as developer to give three fraction A—C in the order of increasing mobility. The least mobile fraction A (18 mg, 7%) was the hydroxamic acid **9**. Fraction B (138 mg, 57%) was the parent alcohol **1**. The most mobile fraction C (6 mg) was an intractable mixture.

*Preparation of 4,4,6-Trimethylcholest-5-en-3$\beta$-ol Nitrite (**4**).* To the 3$\beta$-ol **3** (428 mg) in pyridine (15 ml) cooled by Dry Ice–ethanol, was added nitrosyl chloride (1 cm$^3$). The solution was stirred for 30 min and poured into water and ice. The nitrite was collected by filtration and washed with water. The amount of the nitrite obtained was 440 mg (96%). It melted at 117.0—119.5 °C. This nitrite was recrystallized from acetone to yield an analytical specimen, mp 118.5—120 °C; $[\alpha]^{19}_{D}$ −26.8° (*c* 0.5, $CHCl_3$); IR, 1648 and 1613 (ONO), 801 and 776 cm$^{-1}$ (ONO); $^1$H NMR, $\delta=0.67$ (3H, s, 18-H), 1.05 (3H, s, 19-H), 1.14 and 1.27 (each 3H, each s, 4,4-dimethyl), 1.76 (3H, s, 6-methyl), and 5.12 (1H, dd, $J=5$ and 11 Hz, 3$\alpha$-H); UV (benzene) 386 ($\varepsilon$50), 373 (90), 357 (89), 345 (65), and 334 (48).

*Photolysis of 4,4,6-Trimethylcholest-5-en-3$\beta$-ol Nitrite (**4**) with 373 nm Monochromatic Light.* A solution of the nitrite (260 mg) in dry benzene (3 cm$^3$) in a quartz cell was placed in a chamber of a JASCO CRM-FA grating spectroirradiator and irradiated with 373 nm light for 12 h; complete decomposition of the nitrite had occurred after this period. The solvent was removed under vacuum and the photolysate (271 mg) was subjected to preparative TLC with benzene as developer to give six fractions, A—F in the order of increasing mobility. The least mobile fraction A (24 mg, 13%) was the hydroxamic acid **11**. It crystallized from acetone. Mp 178—181 °C. (Found: *m/z* 457.3907. Calcd for $C_{30}H_{51}NO_2$, M, 457.3919) MS, *m/z* (rel intensity) 457 (M$^+$, 21.9), 442 (M$^+$−$CH_3$, 18.3), 441 (M$^+$−0.69), 440 (M$^+$−OH, 9.5), 427 (M$^+$−2$CH_3$, 11.1), 426 (M$^+$−$CH_3$−O, 339), 369 (100), and 327 (52.6); IR 3400 (br, OH), and 1626 cm$^{-1}$ (amide CO); $^1$H NMR $\delta=0.68$ (3H, s, 18-H), 1.22 (3H, s, 19-H), 1.67 and 1.73 (each 3H, each s, 4a-*gem* dimethyl), and 1.85 (3H, s, 6-methyl).

Fraction B (44 mg, 18%) was identical with the parent 3$\beta$-ol **3**. The fractions C (21 mg), D (15 mg), and E (8 mg) were intractable mixtures. Fraction F (60 mg, 25%) was the seco-aldehyde **10**. It could not be induced to crystallize but its spectroscopic data were identical with those of 4,6-dimethyl-4-methylene-3,4-secocholest-5-en-3-al obtained from the irradiation of 3$\beta$-ol **3** in benzene containing mercury (II) oxide and iodine.[5] [In the mass spectrometric data on compound **10** in the reference 5, 411 (M$^+$−$CH_2CH_2CHO$, 100) should read 411 (M$^+$−$CH_3$, 8.5), 369 (M$^+$−$CH_2CH_2CHO$, 100)].

*Photolysis of 4,4,6-Trimethycholest-5-en-3β-ol Nitrite with a Pyrex-filtered Light.* The nitrite **4** (280 mg) in dry benzene (38 cm$^3$) in a Pyrex vessel was irradiated for 10 h in a nitrogen atmosphere. The solvent was removed by rotary evaporation and the product was subjected to preparative TLC with benzene to yield 3β-ol (47 mg, 18%), 4,4,6-trimethylcholest-5-en-3-one (10 mg, 4%) and seco-aldehyde **10** (16 mg, 6%). No hydroxamic acid **11** was found in the product.

*Preparation of 3α-Methylcholest-5-en-3β-ol Nitrite (**6**).* The 3β-ol **5** (200 mg) in pyridine (6 cm$^3$) was treated with nitrosyl chloride in pyridine in a usual manner to afford a crystalline nitrite, mp 115—117 °C (185 mg, 86%); $[\alpha]^{18}_{D}$ +6.9° ($c$ 0.9, $CHCl_3$); IR 1628 (ONO), 810 (ONO), and 768 cm$^{-1}$ (ONO); $^1$H NMR, $\delta$=0.68 (3H, s, 18-H), 1.07 (3H, s, 19-H), 1.54 (3H, s, 3α-methyl) and 5.45 (1H, br s, 6-H); UV (THF) 400 ($\varepsilon$49), 384 (75), 367 (67), 355 (46), and 342 (27).

*Photolysis of 3α-Methylcholest-5-en-3β-ol Nitrite (**6**) with 384 nm Monochromatic Light.* The nitrite (180 mg) in dry benzene (3 cm$^3$) in a quartz vessel was placed in a chamber of JASCO CRM-FA grating spectroirradiator and was irradiated with 384 nm light for 10.5 h. The solvent was removed under vacuum and the brownish photolysate (155 mg) was subjected to preparative TLC with benzene–diethyl ether (10:1) to give four fractions A—D in the order of increasing mobility. The least mobile fraction A (21 mg, 12%) was the nitroso dimer **13**. This was recrystallized from methanol. Mp 111—113 °C; (Found: M$^+$ 429.3601. Calcd for $C_{28}H_{47}NO_2$: 429.3606); IR 1718 (acetyl) and 1196 cm$^{-1}$; $^1$H NMR, $\delta$=0.66 (3H, s, 18-H), 1.06 (3H, s, 19-H), 2.15 (3H, s, acetyl), 4.65 and 4.86 (each 1H, each d, $J$=13.5 Hz, 4-methylene), and 5.58 (1H, br, s, 6-H) MS, $m/z$ (rel intensity), 429 (1.0), 341 (100, $M^+-CH_3COCH_2-CH_2$), 71 (91.2), 57 (89.2), and 43 (86.2). UV (dioxan) 294 ($\varepsilon$8300). Fraction B (20 mg) was an unidentified gum.

Fraction C (23 mg, 14%) was the parent 3β-ol. The most mobile fraction D (13 mg) was an unidentified gum.

*Photolysis of 3α-Methylcholest-5-en-3β-ol Nitrite (**6**) with Pyrex-filtered Light.* The nitrite (160 mg) in dry benzene (15 cm$^3$) in a Pyrex-vessel was irradiated for 1.5 h. The crude product (173 mg) was subjected to preparative TLC with hexane–diethyl ether (5:1). The TLC plates were developed with the solvent twice to give five fractions A—E in the order of increasing mobility. The least mobile fraction A (110 mg) was again subjected to preparative TLC to afford three fractions $E_1$—$E_3$. Fractions $E_1$ (29 mg) and $E_3$ (112 mg) were not identified. Fraction $E_2$ (34 mg, 21%) was the nitrosodimer **13** which, after recrystallization, was identical with the specimen obtained by monochromatic light photolysis. The fractions B (7 mg), D (6 mg), and E (7 mg) were unidentified gums. Fraction C (27 mg, 18%) was the parent 3β-ol.

*Preparation of 3α,4,4-Trimethylcholest-5-en-3β-ol Nitrite (**8**).* The 3β-ol (330 mg) in pyridine (3 cm$^3$) was treated with nitrosyl chloride–pyridine in a usual manner while the flask was cooled by ice. The solution was poured into water and the solid obtained was collected by filtration to give a gummy nitrite. This was dissolved in diethyl ether and the ethereal solution was dried over anhydrous sodium sulfate. The removal of the solvent gave a crystalline mixture of 3β-ol **7** and the nitrite 8, IR 1622 (ONO), 795 and 760 cm$^{-1}$ (ONO); $^1$H NMR $\delta$=0.68 (s, 18-H of **7** and **8**), 1.05 (s, 19-H of **8**), 1.14 and 1.15 (each s, *gem*-dimethyl group at the C-4 of **8**), 1.52 (s, 3α-methyl of **8**), 5.49 (br s, 6-H of **7**), and 5.56 (br s, 6-H of **8**). The ratio of **7** to **8** estimated by the signal areas of 6-H of **7** and that of **8** was 1:2.4. UV (THF) 398, 382, 366, 353, and 340.

*Photolysis of 3α,4,4-Trimethylcholest-5-en-3β-ol Nitrite (**8**) with 382 nm Monochromatic Light.* The above nitrite (285 mg) in benzene (3 cm$^3$) in a quartz cell was placed in a chamber of CRM-FA grating spectroirradiator and photolyzed with 382 nm light for 5.5 h. The solvent was evaporated and the product was subjected to preparative TLC to give six fractions (A—F) in the order of their mobility on the TLC plate. The most mobile fraction A (24 mg, 13%) was an oily methyl ketone **14** and this was again purified by TLC. (Found: $m/z$ 426.3851. Calcd for $C_{30}H_{50}O$; M, 426.3858); MS, $m/z$ (rel intensity) 426 (M$^+$, 34.6), 383 (18.1), 355 ($M^+-CH_3COCH_2CH_2$, 100), 313 (16.8), 147 (63.4), 133 (31.1) 121 (34.6), 105 (43.6), 95 (48.5), 84 (36.4), 69 (35.8), 57 (44.4), 55 (42.6), and 43 (71.3); IR (neat), 1724 ($CH_3CO$), 1164, and 898 cm$^{-1}$; $^1$H NMR, $\delta$=0.68 (3H, s, $CH_3CO$), 4.47 and 4.84 (each 1H, each br s, 4-methylene), and 5.61 (1H, br d, $J$=4.5 Hz, 6-H) UV (EtOH) 274 ($\varepsilon$ 4000), and 203 (57600).

Fractions B (25 mg), D (8 mg), and F (11 mg) were intractable mixtures. Fraction C (126 mg, 23%) was identical with the parent alcohol **7**. Fraction E (23 mg, 11%) was, after purification by TLC, identified as an amorphous nitroso dimer **15**. MS, $m/z$ (rel intensity) 427 (8.3) 426 (14.4), 355 ($m/z$ 426 $-CH_3COCH_2CH_2$, 41.2) and 43 (100); IR (neat), 1717 ($CH_3CO$), 1541, and 1165 cm$^{-1}$; $^1$H NMR, $\delta$=0.67 (6H, s, 18- and 18′-H), 1.21 (6H, s, 19- and 19′-H), 1.40 (12H, s, *gem*-dimethyl groups at C-4 and C-4′), 2.15 (6H, s, 3- and 3′-methyl), and 5.67 (2H, 6H and 6′-H).

*Photolysis of 3α,4,4-Trimethylcholest-5-en-3β-ol Nitrite with a Pyrex-filtered Light.* The 3β-ol nitrite (485 mg) in benzene (32 cm$^3$) was irradiated for 2.5 h under a nitrogen atmosphere. The product (482 mg) was subjected to preparative TLC with benzene to give 6 fractions A to F in the order of decreasing mobilities. The fraction A (112 mg, 35%) was an oily methyl ketone **14**.

Fraction D (161 mg, 6%) was, after further purification, identical with the parent 3β-ol **7**. Fraction F (54 mg, 16%) was the nitroso dimer **15**.

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