Photoinduced Transformations. Part 60.[1] Photoinduced Rearrangements of Cholesteryl Nitrites with Monochromatic Light

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Photolysis of cholesteryl nitrite in benzene with monochromatic light (λ 389 nm) gave (*E*)-4′-azodi-(3,4-seco-cholest-5-en-3-one) *NN*′-dioxide (9) which was transformed into *N*-hydroxy-4-aza-4a-homocholest-5-en 3-one (10) and 3,3-bisisopropoxy-3,4-secocholest-5-en-4-one oxime (20) in isopropyl alcohol under reflux. Photolysis of the dimer (9) with Pyrex-filtered light gave 3,4-secocholest-5-ene-3,4-dione 4-oxime(25). In contrast, irradiation of 4,4-dimethylcholesteryl nitrite (2) in benzene with monochromatic light gave a good yield of 4a,4a-dimethyl-4-aza-4a-homocholest-5-en-3-one (11) without any accompanying nitroso-dimers. These results as evidence that hydroxamic acids [*e.g.* (10)] obtained from the photolysis of nitrites are formed by thermal cyclization of nitrosointermediates [*e.g.*, (7)].

Although irradiation of the nitrite (2) with Pyrex-filtered light gave a result similar to that with monochromatic light, low yields of the *Z*-isomer (26) of the nitroso-dimer (9) and 3β(4-oxa-4a-homocholest-5-en-3α-yloxy)-cholest-5-ene (27) were isolated from a mixture obtained from the photolysis of cholesteryl nitrite (1) with Pyrex-filtered light. Some notable features in the present results are discussed.

As a part of our studies on the photorearrangements of cyclic homoallyl alcohol nitrites,[2] we have investigated the photoreactions of cholesteryl nitrite (1) and its 4,4-dimethyl derivative (2) with monochromatic light and with Pyrex-filtered light. The results are reported in this paper.

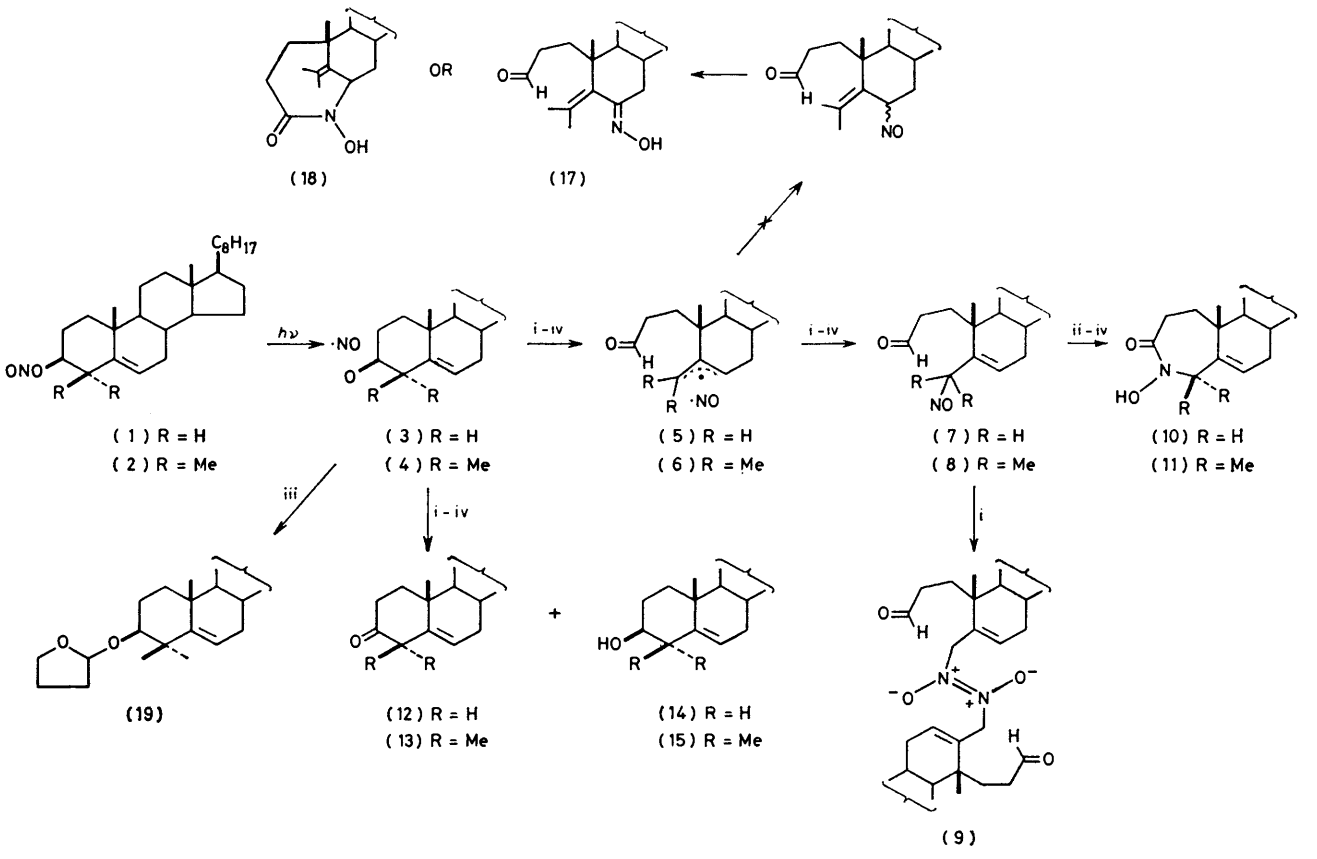
RESULTS

Cholesteryl nitrite (1), prepared by the standard method, was irradiated in dry benzene with 389 ± 8 nm light for 22 h to give four major products, three of which were identified: cholest-5-en-3-one (12) (6%), cholesterol (14) (42%), and the new compound (9) (19%) (Scheme 1). The ketone (12) was isolated after isomerization to cholest-4-en-3-one with base. The molecular formula of compound (9) was confirmed as $C_{54}H_{90}N_2O_4$ by field-desorption (FD) mass spectrometry and elemental analysis. The u.v. spectrum of compound (9) in dioxan shows an absorption maximum characteristic of the $^{-}O-\overset{+}{N}=\overset{+}{N}-O^{-}$ chromophore.[3] This u.v spectrum, together with ^1H and ^{13}C n.m.r., and i.r. spectra, were consistent with the structure (*E*)-4,4′-azodi-(3,4-secocholest-5-en-3-one) *NN*′-dioxide.

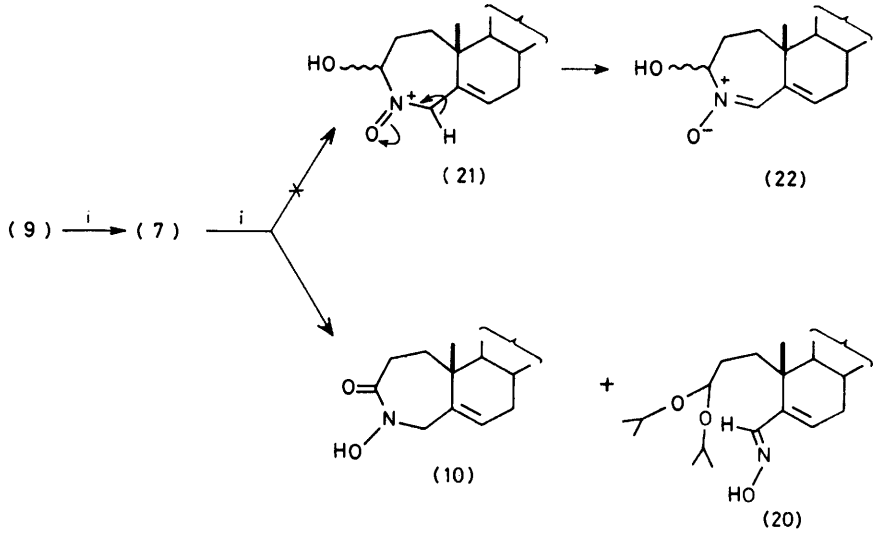
The nitroso-dimer (9) when heated under reflux in isopropyl alcohol for 1 h gave the two compounds (10) and (20) (Scheme 2). High-resolution mass spectrometry proves that compound (10) (17% yield) has the molecular formula $C_{27}H_{45}NO_2$. The low-resolution mass spectrum shows a peak at *m/e* 399, assigned to an ion which results from loss of a hydroxyamino-oxygen from the molecular ion.[4] These results, together with i.r. and ^1H n.m.r. spectra, are consistent with the structure *N*-hydroxy-4-aza-4a-homocholest-5-en-3-one (10). High-resolution mass spectrometry shows that compound (20) (16% yield) has the molecular formula $C_{33}H_{59}NO_3$ and electron-impact mass spectrometry shows an intense fragment ion at *m/e* 131, assigned to the fragment $Me_2CHOCH=\overset{+}{O}CHMe_2$.[5] On the basis of this mass spectrum together with the i.r., u.v., and ^1H n.m.r. spectra, 3,3-bis-isopropoxy-3,4-secocholest-5-en-4-one oxime (20) was assigned as the structure.

When the nitroso-dimer (9) in a mixture of diethyl ether and methanol, which contained 2M hydrochloric acid, was stirred at room temperature the crystalline compounds (23) (42% yield) and (24) (14% yield were obtained (Scheme 3). They were identified on the basis of their u.v., ^1H n.m.r. and mass spectra. The mass spectrum of compound (23) shows a weak peak at *m/e* 75, assigned to the fragment $MeO-CH=\overset{+}{O}Me$. The molecular formula of compound (24) was determined as $C_{29}H_{51}NO_3$ by high-resolution mass spectrometry and the low-resolution mass spectrum shows a base peak at *m/e* 75, attributable to the fragment $MeO-\overset{+}{C}H=OMe$. The 389 nm light did not further transform the dimer (9) and thus photolysis of (9) with Pyrex-filtered light in benzene was undertaken. The major product of this photolysis was found to be 3,4-secocholest-5-ene-3,4-dione 4-oxime (25) which was obtained as the dimethylacetal (24) in 38% yield by extraction from t.l.c. plates with methanol–dichloromethane. The oxime (25) is formed by dissociation of (9) into the nitroso-monomer (7), followed by isomerization (Scheme 4).

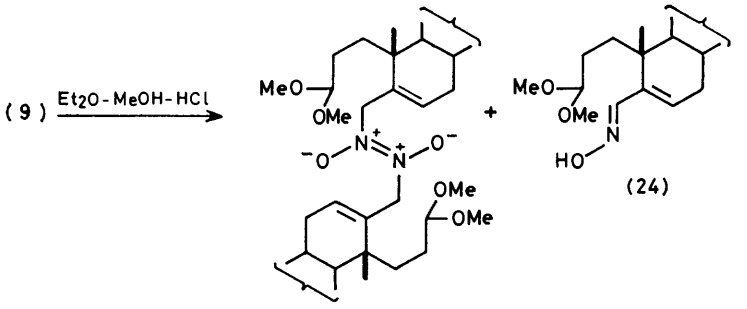
We then examined the effects of alkyl groups attached to the carbon atom adjacent to the carbon atom carrying the ONO group. 4,4-Dimethylcholesteryl nitrite (2), prepared by the standard method and dissolved in dry benzene, was photolysed with monochromatic light (λ 375 nm) until all the nitrite was decomposed. This photolysis gave three products, 4,4-dimethylcholest-5-en-3-one (13)[6] (8% yield), 4 4-dimethylcholesterol (15) (25% yield) and the new compound (11). High-resolution mass spectrometry of compound (11) (38% yield) indicated that it had the molecular formula $C_{29}H_{49}NO_2$ and the structure was found to be *N*-hydroxy-4a,4a-dimethyl-4-aza-4a-homocholest-5-en-3-one by spectroscopy. An alternative structure (18) (Scheme 1) was excluded on the basis of the ^{13}C n.m.r. spectrum which showed a signal at δ 66.5 p.p.m., assignable to an sp^3-carbon atom bearing a nitrogen atom, two signals arising from sp^2-carbon atoms at δ 127.6 and 145.7 p.p.m., and a signal arising from the carbonyl group of hydroxamic acid at δ 171.4 p.p.m. By the aid of off-resonance decoupling, the two signals at δ 66.5 and 127.6 p.p.m. were confirmed to be due to a quaternary carbon atom and an sp^2-carbon atom bearing a hydrogen atom. Thus, the signals at δ 145.7 and 66.5 p.p.m. can be assigned to C-6, C-5, and C-4a in the hydroxamic acid (11).



SCHEME 1 For R = H. *Reagents:* i, C_6H_6, λ 389 nm. For R = Me. *Reagents:* ii, C_6H_6, λ 375 nm; iii, tetrahydrofuran (THF), λ 372 nm; iv, C_6H_6, λ > 300 nm

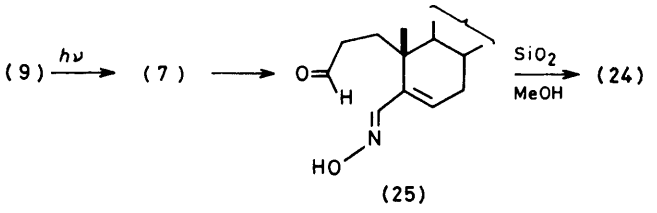


SCHEME 2 *Reagents:* i, Pr^iOH, reflux



SCHEME 3

The photolysis of the nitrite (2) in THF, as hydrogen-donating solvent, gave a lower yield (29%) of the hydroxamic acid (11) together with the ketone (13) (9% yield), a much greater yield (30%) of the alcohol (15), and a new product (19). The structure of the new product (19) (7% yield) was ascertained as 4,4-dimethyl-3β-tetrahydrofuran-2-yloxy cholest-5-ene, which arises *via* hydrogen abstraction from

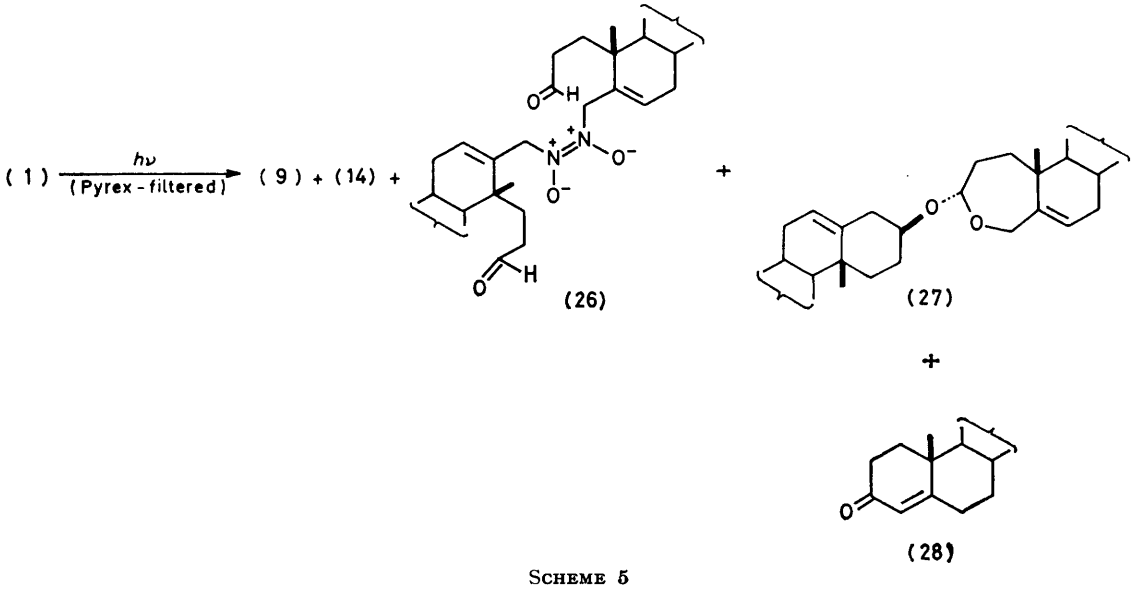


SCHEME 4

the solvent by the 3β-oxyl radical (4). The molecular formula of compound (19) was determined as $C_{33}H_{56}O_2$ by high-resolution mass spectrometery. The i.r. spectrum showed the absence of bands arising from carbonyl- and hydroxy-groups and the presence of a band due to the ether linkage. The n.m.r. spectrum showed a two-proton broad singlet and a one-proton double doublet assigned to methylene and methine protons in the tetrahydrofuranyl group. The mass spectrum showed a base peak at *m/e* 71 attributable to the ion (A).

(A)

We finally examined the products from the photolysis of both nitrites (1) and (2) in benzene with Pyrex-filtered light and compared them with those from monochromatic light photolysis. Irradiation of cholesteryl nitrite with Pyrex-filtered light gave a mixture from which five compounds, 3β-(4-oxa-4a-homocholest-5-en-3α-yloxy)cholest-5-ene (27)[7] (4% yield), cholesterol (14) (16% yield), cholest-4-en-3-one (28) (4% yield), the (E)-nitroso-dimer (9) (11% yield), and the (*Z*)-nitroso-dimer (26) (3% yield) were separated by extensive column chromatography and preparative t.l.c. (Scheme 5). The acetal (27) was identified by direct comparison with a specimen [7] obtained from the thermal rearrangement of cholesteryl hypoiodite in benzene which contained mercury(II) oxide and iodine. Cholest-4-en-3-one (28) should be formed by isomerization of cholest-5-en-3-one during the course of the separation. Compound (26) was assigned the structure of the (*Z*)-nitroso-dimer by spectro



SCHEME 5

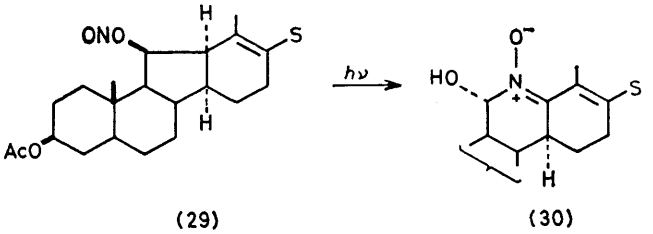
scopy (see Experimental section). Irradiation of 4,4-dimethylcholesteryl nitrite (2) in benzene with Pyrex-filtered light, on the other hand, gave nearly the same results as in the case of the monochromatic-light photolysis. 4,4-Dimethylcholest-5-en-3-one(13) (6% yield), 4,4-dimethylcholesterol (15) (26% yield), and the 4-aza-4a-homocholestenone (11) (43% yield) were obtained as the products (Scheme 1).

DISCUSSION

The photoinduced rearrangement of cycloalkyl nitrites to cyclic hydroxamic acids was first found with several steroidal 17β-ol nitrites by Barton and his co-workers.[8]

The present results show that, as might be expected, seven-membered cyclic hydroxamic acids can be prepared from steroidal cyclohexyl nitrites by this photorearrangement, provided that an intermediate oxyl radical [*e.g.* (3)] is susceptible to β-scission. In the nitrites (1) and (2), β-scission of the oxyl radical is aided by the presence of a double bond at C-5, which stabilizes the C-radical [*e.g.*, (5)] resulting from the β-scission or the preceding transition state. The effect of *gem* dimethyl groups on C-4 for the β-scission is apparent since photolysis of the nitrite (2) gave the product (11) (40% yield), which arises from the β-scission, whereas photolysis of the nitrite (1) gave only *ca.* 20% yield of the product (9), which arises from the β-scission. This photochemical rearrangement of steroidal cyclopentyl nitrites to hydroxamic acids may involve cyclization of a nitroso-aldehyde intermediate [*e.g.* (7)].[2a,8,9] Our recent studies have demonstrated [9] that the cyclization of the nitroso-aldehyde intermediate is a thermal process and does not involve excited species of the nitroso-compound [*e.g.* (7) or (8)], despite a claim by other investigators.[10] Since thermal dissociation of the nitroso-dimer into monomeric nitroso-compounds has been established,[11] we believe that isolation of the nitroso-dimer (9) from the photolysis of cholesteryl nitrite (1) and its thermal cyclization to the hydroxamic acid (10) can be taken as more definite evidence for our previous conclusion.[9]

The possibility that the hydroxamic acid (10) is formed from an oxime–aldehyde [(25) in Scheme 6], generated by isomerization of the nitroso-aldehyde (7), has been excluded because of the failure of thermal cyclization of an oxime–aldehyde obtained by the photolysis of a fused cyclopentyl nitrite.[2a]



(29) (30)

It is of interest to note that, while the photoinduced reaction of the homoallyl alcohol nitrite (29) led exclusively to the α-hydroxynitrone (30)[2a], the thermal cyclization of the nitroso-dimer (9) gave the hydroxamic acid (10), despite the presence of mobile allylic hydrogen atoms. Examination of the Drieding model of the corresponding nitrone (22) (Scheme 2) indicates that the C=N and C=C bonds can not effectively be conjugated in this 6/7 fused system and little stabilization by conjugation to the nitrone from the intermediate (21) can be expected. This may be an important reason for the exclusive formation of the hydroxamic acid (10).

It should also be noted that whereas irradiation of the nitrite (2) afforded the hydroxamic acid (11) without any accompanying formation of a nitroso-dimer corresponding to compound (9), irradiation of cholesteryl nitrite (1) does not give the hydroxamic acid (10) but, rather, the nitroso-dimer (9). A probable reason for this difference would be that a bimolecular reaction of the nitroso-intermediate (8) to give the nitroso-dimer is hindered in the photoreaction of the nitrite (2) owing to the presence of the 4,4-dimethyl groups.

Interestingly, no products [*e.g.* (17) and/or (18)] which arise by combination of nitric oxide with the less substituted C-6 terminus of the allyl radical intermediate (6) were found in the photolysis of the nitrite (2).

The acetal (27) has only been obtained in the photolysis of cholesteryl nitrite with Pyrex-filtered light. Repeated, careful experiments confirmed that photolysis of cholesteryl nitrite with monochromatic light or photolysis of the nitroso-dimer (9) with Pyrex-filtered light does not give the acetal (27). The reason for this difference is not clear at present. The pathway to the acetal (27) has been discussed in an earlier paper.[7]

EXPERIMENTAL

Instruments and general procedures are described in an earlier paper.[7] The low-resolution mass spectra of compounds (9), (10), (11), (19), and (23) were recorded by Miss Y. Chiba of the Faculty of Agriculture and those of compounds (20) and (24) by the staff of the Faculty of Pharmaceutical Sciences, Hokkaido University, with a Hitachi JMS-D 300 spectrometer (70 eV). The high-resolution mass spectra of compounds (19), (20), and (24) were recorded by Miss Y. Chiba with a Hitachi JMS-D 300 spectrometer and those of compounds (10) and (11) by Mr. T. Katoh, Coal Research Laboratory of this Faculty, with a Hitachi R Mu 7MF double-focussing mass spectrometer (70 eV).

Preparation of Cholesteryl Nitrite (1).—To cholesterol (2.1 g) in pyridine (20 ml) was added a pyridine solution of nitrosyl chloride (1 ml). The mixture was stirred for 40 min at −10 °C and poured into ice–water. Cholesteryl nitrite was filtered off, washed with water, and dried. The nitrite (1) (2.2 g) had m.p. 97.5—100.5 °C; $\nu_{max.}$ 788, 825, 866 (ON), 1 136, and 1 603 and 1 640 cm^{-1} (NO); τ 9.32 (3 H, s, 18-H), 8.95 (3 H, s, 19-H), 4.71 br (1 H, 3α-H), and 4.55br (1 H, 6-H); $\lambda_{max.}$ (benzene) 236 nm (ε 47), 247 (63), 259 (79), 272 (78), and 288 (inflection, 52).

Photolysis of Cholesteryl Nitrite (1) *with Monochromatic Light* (λ 389 ± 8 nm).—The nitrite (1) (350 mg) in dry benzene (3 ml) was irradiated for 22 h with 389 ± 8 nm light generated by a CRM-FA grating spectroirradiator equipped with a 2-kW Xe arc. The solvent was evaporated and the residue subjected to preparative t.l.c. with hexane–diethyl ether (2 : 3) to afford 4 fractions: A (33 mg), B (33 mg), C

(137 mg), and D (68 mg), given in order of decreasing mobility. Fraction A was a mixture and was dissolved in a few ml of 5% methanolic potassium hydroxide–tetrahydrofuran (THF) (1 : 1) and stirred at room temperature for 2 h. The solution was neutralized with 2M hydrochloric acid and worked up as usual. The residue showed 5 spots on t.l.c. with benzene and was subjected to preparative t.l.c. with benzene to give cholest-4-en-3-one (n.m.r.) (19 mg, 6%) as the major product. Fraction B was not identified, fraction C (42%) was cholesterol and fraction D (19%) was recrystallized from acetone to give (*E*)-4,4′-*azodi*-(3,4-*secocholest*-5-*en*-3-*one*) NN′-*dioxide* (9) as crystals, m.p. 98—98.5 °C; $[\alpha]_D^{26}$ −12.8 ° (*c* 0.87 $CHCl_3$); *m/e* [field desorption (FD)] 830 (M^+, 0.7), 818 (0.7), 815 (0.7), 802 (0.8), 801 (0.8), 800 (1.0), 798 (0.7), 794 (1.0), 788 (0.7), 785 (0.7, 751 (0.8), 702 (1.4), 608 (1.5), 415 (100), and 385 (41.2) (Found: C, 78.05, H, 10.65, N, 3.35. $C_{54}H_{90}N_2O_4$ requires C, 78.02; H, 10.91; N, 3.37%); $\nu_{max.}$ 1 731 (formyl) and 1 198 cm^{-1}; $\lambda_{max.}$ (dioxan) 296 nm (ε 7 500); τ 9.34 (6 H, s, 18-H and 18′-H), 8.93 (6 H, s, 19-H and 19′-H), 5.33 and 5.12 (each 2 H and d, 4- and 4′-H), 4.31br (2 H, d, 6 and 6′-H), and 0.25br (2 H, s, $W_{\frac{1}{2}}$ 3.0 Hz, 3 and 3′-H); *m/e* 431 (0.1), 430 (0.2), 415 (26.0), 400 (17.9), 399 (21.4), 398 (100), 382 (13.1), 358 (10.0), 95 (20.3), 81 (17.6), 69 (19.6), 57 (26.0), 55 (34.1), 43 (34.7), and 41 (20.0); δ ($CDCl_3$, 22.63 MHz, tetramethylsilane) 201.7 (C-3 and C-3′), 76.3 (C-4 and C-4′), 132.7 (C-5 and C-5′), and 129.1 (C-6 and C-6′).

Thermal Decomposition of the Nitroso-Dimer (9) *obtained from Cholesteryl Nitrite* (1).—The nitroso-dimer (9) (142 mg) in isopropyl alcohol (20 ml) was refluxed for 1 h under a nitrogen atmosphere. After the removal of the solvent, the residue was subjected to preparative t.l.c. with hexane–diethyl ether (1 : 2) to give five fractions, A—E, in order of decreasing mobility. Fraction A (28 mg, 16%) was again purified by preparative t.l.c. with hexane–ethyl acetate (8 : 1.5) to yield the oily 3,3-*bisisopropoxy*-3,4-*secocholest*-5-*en*-4-*one oxime* (20) (Found: *m/e* 517.4499. $C_{33}H_{59}NO_3$ requires M^+, 517.4494); $[\alpha]_D^{22}$ −22.6° (*c* 0.5, $CHCl_3$); $\lambda_{max.}$ (ethanol) 233 nm (ε 15 200); $\nu_{max.}$ 3 350 (OH), 1 123, and 1 027 cm^{-1}; τ 2.31 (1 H, s, 4-H), 3.91 (1 H, d, *J* 5 Hz, 6-H), 5.51 (1 H, t, *J* 5.9 Hz, 3-H), 6.16 (2 H, m, two CH of Pr^i), 8.89 (12 H, d, *J* 6.0 Hz, 4 × Me of Pr^i, 8.80 (3 H, s, 19-H), and 9.32 (3 H, s, 18-H); *m/e* 517 (M^+, 0.7%), 382 (23.9), 381 (21.6), 131 [72.3, $Me_2CHOCH{=}\overset{+}{O}{-}CHMe_2$], 99 (47.1), 89 (100), 57 (47.1), 45 (61.9), and 43 (51.6).

Fraction E (25 mg, 17%) gave N-*hydroxy*-4-*aza*-4a-*homocholest*-5-*en*-3-*one* (10) (recrystallized from methanol), m.p. 161.5—164.0 °C; $[\alpha]_D^{25}$ +18° (*c* 1.0, $CHCl_3$) (Found: *m/e* 415.3383. $C_{27}H_{45}NO_2$ requires M^+, 415.3447); $\nu_{max.}$ 3 330br (OH) and 1 619 cm^{-1} (C=O); τ 4.14 (1 H, d, *J* 4.5 Hz, 6-H), 5.63 and 6.18 (each 1 H, d, *J* 13.5 Hz, 4a-H), 8.89 (3 H, s, 19-H), and 8.32 (3 H, s, 18-H); *m/e* 415 (M^+, 100), 399 (M^+ − O, 14.1), 398 (M^+ − OH, 33.7), 371 (14.8), 370 (72.3), 369 (76.9), 55 (48.4), and 43 (38.3).

Photolysis of the Nitroso-dimer (9) *obtained from Cholesteryl Nitrite* (1).—The nitroso-dimer (9) (128 mg) in dry benzene (6 ml) was irradiated through a Pyrex-filter with a 100-W high-pressure Hg arc for 10 h. The solvent was evaporated and the residue was subjected to preparative t.l.c. The t.l.c. plates were developed with diethyl ether–benzene (1 : 1) and each fraction was extracted with dichloromethane, which contained methanol (5%), to afford four fractions: A (7 mg), B (54 mg), C (6 mg), and D (10 mg). Fraction B (38%) was the α,β-unsaturated oxime (24) which, after purification, was identical with a specimen obtained by the reaction of the nitroso-dimer (9) with methanolic hydrochloric acid (see below). Fractions A and C were unidentified gums. Fraction D (8%) was the recovered dimer (9).

Reaction of the Nitroso-dimer (9) *with Methanolic Hydrochloric Acid*.—To the nitroso-dimer (9) (70 mg) in a mixture of methanol (20 ml) and diethyl ether (10 ml) was added 2M hydrochloric acid (0.1 ml). The solution was stirred for 5 h at room temperature, extracted with diethyl ether, the ethereal extract was washed twice with water and dried (Na_2SO_4). Removal of the solvent gave a residue (71 mg) which was recrystallized from acetone–methanol to give 3,3,3′,3′-*tetramethoxy*-4,4′-*azodi*-(3,4-*secocholest*-5-*ene*)NN′-*dioxide* (23) (33 mg, 42%), m.p. 108.5—109.5 °C (98—102 °C before recrystallization); $[\alpha]_D^{20}$ −7.2° (*c* 1.2, $CHCl_3$) (Found: C, 75.0; H, 11.25; N, 2.61. $C_{58}H_{102}N_2O_6$ requires C, 75.43; H, 11.15; N, 3.03%); $\lambda_{max.}$ (dioxan) 296 nm (ε 6 600); $\nu_{max.}$ 726, 1066, 1 126, and 1 195 cm^{-1}; τ 9.32 (6 H, s, 18-H and 18′-H), 8.95 (6 H, s, 19-H and 19′-H), 6.70 (6 H, s, MeO), 6.67 (6 H, s, MeO), 5.68br (2 H, s, $W_{\frac{1}{2}}$ 9.0 Hz, 3- and 3′-H), 5.99 and 6.35 (each 2 H, d, *J* 13.5 Hz, 4- and 4′-H), and 4.38 (2 H, d, *J* 4.2 Hz, 6-H and 6′-H); *m/e* 461 (2.7), 444 (4.9), 429 (17.3), 412 (31.7), 399 (20.3), 382 (12.1), 101 (20.6), 75 ($MeO{-}CH{=}\overset{+}{O}Me$, 100), and 71 (12.6).

The filtrate from the recrystallization was evaporated to give a residue which was subjected to preparative t.l.c. with hexane–diethyl ether (3 : 4). The most mobile fraction (11 mg, 14%) was recrystallized from methanol to give 3,3-*dimethoxy*-3,4-*secocholest*-5-*en*-4-*one* oxime (24) (3 mg), m.p. 112.5—114.5 °C (Found: *m/e* 461.3872. $C_{29}H_{51}NO_3$ requires M^+, 461.3867); $\nu_{max.}$ 3 300 (OH), 1 290, 1 134, 1 042, 947, 835, and 724 cm^{-1}; τ 9.33 (3 H, s, 18-H), 8.89 (3 H, s, 19-H), 6.75 and 6.72 (each 3 H, s, MeO), 5.72 (1 H, t, *J* 4.5 Hz, 3-H), 3.95 (1 H, d, *J* 6.0 Hz, 6-H), and 2.40 (1 H, s, 4-H); $\lambda_{max.}$ (ethanol) 233 nm (ε 14 800); *m/e* 461 (M^+, 0.4%), 412 (4.1), 101 (10.1), 75 ($MeO{-}CH{=}\overset{+}{O}Me$, 100), and 71 (41.5).

Preparation of 4,4-*Dimethylcholesteryl Nitrite* (2).—To 4,4-dimethylcholesterol (15) (414 mg) in pyridine (15 ml) cooled by solid CO_2–ethanol was added, as drops, nitrosyl chloride in pyridine. The solution was stirred for 30 min and poured into water–ice. The crystals were filtered off, washed with water, dried, and evaporated to give the nitrite (2) (440 mg, 99%), m.p. 137—140 °C and, after recrystallization from methanol m.p. 140—141.5 °C; $[\alpha]_D^{21}$ −52.8° (*c* 0.9, $CHCl_3$); $\lambda_{max.}$ (THF) 386 nm (ε 41), 372 (78), 357 (64), 364 (47), and 335 (33); $\lambda_{max.}$ (benzene) 388 nm (ε 43), 375 (72), 361 (70), 348 (53), and 337 (37); $\nu_{max.}$ 1 642 and 1 606 (NO), and 777 and 812 cm^{-1} (ON); τ 9.32 (3 H, s, 18-H), 9.92 (3 H, s, 19-H), 8.90 and 8.86 (each 3-H, s, 2 × 4-Me), 4.92 (1 H, dd, *J* 5.3 and 15.0 Hz), and 4.35 br (1 H, s, 6-H).

Photolysis of the Nitrite (2) *in Benzene with Monochromatic Light* (λ 375 ± 4 nm).—The nitrite (2) (100 mg) in dry benzene (3.5 ml) was irradiated with monochromatic light (λ 375 ± 4 nm) for 10 h. After removal of the solvent, the residue (112 mg) was subjected to preparative t.l.c. with benzene to give four fractions: A (7 mg), B (6 mg), C (23 mg), and D (38 mg). The most mobile fraction, A, was 4,4-dimethylcholest-5-en-3-one (13). The third most mobile fraction, C, was 4,4-dimethylcholesterol (15). The least mobile fraction was N-*hydroxy*-4a,4a-*dimethyl*-4-*aza*-4a-*homocholest*-5-*en*-3-*one* (11) (recrystallized from acetone), m.p. 153—156 °C; $[\alpha]_D^{19}$ +28.4° (*c* 0.9, $CHCl_3$) (Found: *m/e* 443.3688. $C_{29}H_{49}NO_2$ requires M^+, 433.3759); $\nu_{max.}$ 3 120 (OH) and 1 649 cm^{-1} (hydroxamic C=O); τ 9.29 (3 H, s, 18-H), 8.76 (3 H, s, 19-H), 8.40 and 8.33 (each 3 H, s, 2 ×

4a-Me), and 3.92 (1 H, dd, J 1.5 and 6.0 Hz, 6-H); for ^{13}C n.m.r. see text; *m/e* 443 (M^+, 19.1), 428 (M^+ — Me, 100) 427 (M^+ — OH, 9.2), 412 (M^+ — MeO, 16.9), 411 (18.8), 400 (13.6), 355 (32.7), 147 (19.5), 95 (26.7), 57 (30.2), 55 (34.2), and 43 (38.7).

Photolysis of the Nitrite (2) *in THF with Monochromatic Light* (λ372 ± 4 nm).—The nitrite (2) (98 mg) in dry THF (3.5 ml) in a quartz cell (10 × 10 × 45 mm) was placed in a chamber of a JASCO CRM-FA grating spectroirradiator equipped with a 2-kW Xe arc and was irradiated with 372 ± 4 nm light for 10.5 h. After removal of the solvent, the residue (103 mg) was subjected to preparative t.l.c. with benzene–diethyl ether (20 : 1) to give five fractions: A (7 mg), B (8 mg), C (10 mg), D (27 mg), and E (28 mg). Fraction A was *4,4-dimethyl-3β-tetrahydrofuran-2-yloxycholest-5-ene* (19) (recrystallized from methanol), m.p. 117—120 °C (Found: *m/e* 484.4263. $C_{33}H_{56}O_2$ requires M^+, 484.4278); $\nu_{max.}$ 1 090 and 1 038 cm^{-1}; τ 9.35 (3 H, s, 18-H), 8.98 and 8.93 (each 3 H, s, 2 × 4-Me), 8.93 (3 H, s, 19-H), 6.85br (1 H, s, 3α-H), 6.14br (2 H, s, $W_{\frac{1}{2}}$ 15 Hz, 5′-CH_2), 4.77 (1 H, dd, J 1.5 and 13.2 Hz, 2′-H), and 4.46br (1 H, s, 6-H); *m/e* 484 (M^+, 0.1), 428 (0.6), 414 (0.8), 413 (1.2), 412 (0.9), 398 (1.0), 397 (0.7), 396 (1.2), 395 (0.8), 381 (0.8), 370 (0.9), 358 (0.8), 357 (1.9), 356 (1.7), 71 (100), and 43 (10.2). Fractions B and D were the cholesterone (13) and the cholesterol (15), respectively. Fraction E was the 4-aza-4a-homocholesterone (11).

Photolysis of Cholesteryl Nitrite (1) *with Pyrex-filtered Light.*—The nitrite (1) (2.7 g) in dry benzene (160 ml) was irradiated through Pyrex with a 100-W high-pressure Hg arc for 6 h. The solvent was removed and the amorphous residue was subjected to column chromatography (Wako gel C-200, 70 g). Elutions with hexane–benzene (2 : 1) gave a fraction (97 mg) which was identical with 3β-(4-oxa-4a-homocholest-5-en-3α-yloxy)cholest-5-ene (27) (recrystallized from acetone) m.p. 219—220 °C. Elution with hexane–benzene (1 : 3) gave cholesterol (475 mg) and further elution with benzene gave a fraction (399 mg) which was subjected to preparative t.l.c. with hexane—diethyl ether (2 : 3) to give cholest-4-en-3-one (110 mg, 4%). Further elution with benzene–diethyl ether (9 : 1) afforded a mixture (810 mg) which was subjected to preparative t.l.c. with hexane–diethyl ether (1 : 2) to give two fractions: A (180 mg) and B (308 mg). The less mobile fraction B was nitroso-dimer (9) which was recrystallized from acetone. Further elution of the column afforded the most polar crystalline fraction (270 mg) which was subjected to preparative t.l.c. with hexane–diethyl ether (1 : 2) to give four fractions. The least mobile fraction (82 mg) was (*Z*)-*4,4′-azodi-(3,4-secocholest-5-en-3-one) NN′-dioxide* (26) (recrystallized from acetone), m.p. 139.5—141.0 °C; $[\alpha]_D^{23}$ −53° (*c* 1.0, $CHCl_3$); τ 9.31 (6 H, s, 18- and 18′-H), 8.94 (6 H, s, 19- and 19′-H), 5.37 (4 H, unsymmetrical t, J 10.5 Hz, 4 and 4′-CH_2), 4.05 and 4.33 (each 1 H, d, J 4.5 Hz, 6- or 6′-H and 6- or 6′-H), and 0.26 (2 H, d, J 1.2 H, 3- and 3′-H); $\nu_{max.}$ no OH band, 1727 (CHO), 1 011, 991, and 963 cm^{-1}.

Photolysis of the Nitrite (2) *in Benzene with Pyrex-filtered Light.*—The nitrite (2) (400 mg) in dry benzene was irradiated with a 100-W high-pressure Hg arc under an atmosphere of nitrogen for 2.5 h. After the removal of the solvent at < 30 °C the amorphous residue was subjected to preparative t.l.c. with benzene to yield 7 fractions: A (18 mg), B (11 mg), C (22 mg), D (12 mg), E (18 mg), F (98 mg), and G (170 mg) in order of decreasing mobility. Fraction C was the parent ketone (13), fraction F the starting 3β-ol (15), and fraction G the 4-aza-4a-homocholest-5-en-3-one (11).

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