The Photochemistry of Steroidal 6-Membered Cyclic α-Nitro Ketones[1)]

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The results of the photolysis of five steroidal 6-membered cyclic α-nitro ketones in ethanol are described. Irradiation with a Pyrex-filtered light of 2-nitro-5α-cholestan-3-one in ethanol, which exists exclusively in the enol form in the solvent, resulted in a new photorearrangement and gave 5α-cholestane-2,3-dione 3-oxime with the accompanying formation of the corresponding α-diketone. We propose a path involving a nitro–nitrite rearrangement for this anomalous formation of 5α-cholestane-2,3-dione 3-oxime. However, similar irradiation of 4,4-dimethyl-2-nitro-5α-choloestan-3-one, which exists exclusively as the enol form in ethanol, and 3-nitro-5α-cholestan-2-one, which is in an 1:1 equilibrium mixture of keto and enol forms in ethanol, gave the corresponding α-hydroxyimino ketone and α-diketone respectively. Irradiation of 4β-nitro-5β-cholestan-3-one and 6α-nitro-5α-cholestan-7-one, both of which exist as the keto form in ethanol, gave similarly the corresponding α-hydroxyimino ketone respectively, but without the accompanying formation of α-diketone. The α-hydroxyimino ketones from the above four 6-membered cyclic α-nitro ketones arise through the hydrogen abstraction by the n,π* excited nitro group of the keto forms of the α-nitro ketones followed by the elimination of the element of water, while α-diketones are formed via the nitro–nitrite rearrangement of the excited nitro group of the enol forms.

In connection with our studies of nitrite photolysis[2)] and of photoinduced nitro–nitrite rearrangement,[3)] we have been interested, too, in the photochemistry of cyclic α-nitro ketones.

In this paper, we report the photochemistry of five steroidal 6-membered cyclic α-nitro ketones, three of which exist in solution predominantly in their enol form. The photochemistry of cyclic α-nitro ketones which in solution exist in their keto forms has been reported by Reid and Tucker, who found that 2-nitrocycloheptanone and α-nitro camphor rearrange to give cyclic *N*-hydroxy imides and α-hydroxyimino ketones on irradiation in solution.[4)]

Results

Preparations and Structures of the α-Nitro Ketones. Five steroidal 6-membered cyclic α-nitro ketones, 2-nitro-5α-cholestan-3-one (**3**)[5,6)] 4,4-dimethyl-2-nitro-5α-cholestan-3-one (**4**), 3-nitro-5α-cholestan-2-one (**11**), 4β-nitro-5β-cholestan-3-one (**13**), and 6α-nitro-5α-cholestan-7-one (**17**),[6)] chosen for the present study, were prepared by mononitration of the corresponding steroidal ketones with alkyl nitrate and bases.[7,8)]

We found that nitration of 5α-cholestan-3-one (**1**) under the conditions reported by previous investigators [butyl nitrate (3.35 mol) and potassium *t*-butoxide (5.78 mol) in *t*-butyl alcohol at 17—20 °C][5)] led to the substantial formation of α,ω-dinitro secosteroid; this arose from the hydrolytic cleavage of the dipotassium salt of α,α′-dinitro ketone.[9)] The formation of α,ω-dinitro secosteroid as a by-product in the nitration of ketone **1** with an excess of ethyl nitrate and potassium *t*-butoxide in THF at −40—0 °C has also been reported by Meakins and his colleagues.[6)] We found that the formation of the α,ω-dinitro secosteroid that is formed by the hydrolysis of the dipotassium salt of 2,4-dinitro-5α-cholestan-3-one can be avoided; no α,ω-dinitro secosteroids or ω-nitro carboxylic esters[7)] that arise from cleavage reactions were found in the products when a lesser amount of a base was used [propyl nitrate (2.9 mol) and potassium *t*-butoxide (2.6 mol)].

All five steroidal 2-nitro ketones are crystalline compounds. The IR spectra of 2-nitro-5α-cholestan-3-one (**3**) in Nujol exhibited strong bands at 1616 and 1513 cm^{-1} due to the carbon–carbon double bond and a conjugated nitro group. There were also very weak bands at 1746 and 1561 cm^{-1} owing to the carbonyl and a nonconjugated nitro group. 2-Nitro-5α-cholestan-3-one (**3**) seems therefore to exist almost exclusively as its enol form in the mulled state although a small portion exists as the keto form.[10)]

The absence of any bands due to the presence of non-conjugated 2-nitro ketone indicates that 4,4-dimethyl-2-nitro-5α-cholestane (**4**) in the mulled state exists exclusively in its enol form. The IR spectrum of 3-nitro-5α-cholestan-2-one (**11**) in Nujol exhibited two bands at 1619 and 1509 cm^{-1} due to the conjugated nitro group, and two bands at 1735 and 1562 cm^{-1} due to the carbonyl and nonconjugated nitro groups. It is clear that this nitro ketone in the mulled state exists as an equilibrium mixture of the keto and enol forms. On the other hand, the IR spectra of 4β-nitro-5β-cholestan-3-one (**13**) and 6α-nitro-5α-cholestan-7-one (**17**) indicated that these ketones in the mulled state exist almost exclusively in their keto form (Table 1).

The ^1H NMR spectra of 2-nitro-5α-cholestan-3-one (**3**) and its 4,4-dimethyl derivative (**4**) in $CDCl_3$ indicated that these 2-nitro ketones in the solution exist entirely as their enol form (see Experimental). It thus becomes apparent that these 2-nitro ketones in a more polar protic solvents such as the ethanol used in the present photolysis exist exclusively in their enol form.

In contrast to the behavior of these 2-nitro ketones,

Table 1. Infrared Absorptions of Cyclic α-Nitro Ketones[a]

α-Nitro ketone	Absorptions of functional groups (cm^{-1})	
	HO-C=C-NO_2	O=C-CH-NO_2
3	1513 and 1616	1561[b] and 1746[b]
4	1513 and 1605	—
11	1509 and 1619	1562 and 1735
13	—	1558 and 1714
17	—	1558 and 1728

a) In Nujol mull. b) A very weak band.

the ^1H NMR spectrum of 3-nitro-5α-cholestan-2-one (**11**) in $CDCl_3$ exhibited the presence of signals assignable to the 3α-H of its keto form (see Experimental) and indicated that it exists in an equilibrium with the enol form in $CDCl_3$. The ^1H NMR spectrum of **11** in methanol exhibited a singlet at δ 0.69 and a doublet of a doublet at δ 5.60 (J=7.2 and 11.9 Hz); these were assignable to the 18-H and the 3α-H of its keto form respectively; there was also a singlet at δ 0.71, assignable to the 18-H of its enol form. The ratio of the keto and enol forms in methanol estimated by their signal area was 45.5:54.5.

The ^1H NMR spectra of 4β-nitro-5β-cholestan-3-one (**13**) and 6α-nitro-5α-cholestan-7-one (**17**)[6] in $CDCl_3$ indicated that in solution they exist exclusively in their keto forms.

The aliphatic nitro group is known to exhibit two absorption bands, one in 210 nm and another in the 270—280 nm region.[11] The band at the lower wavelengths with a low intensity is due to the n→π* transition while the 210 nm band is due to the π→π* transition.[12-14] The α,β-unsaturated nitro compounds, on the other hand, are known to show absorption maxima with high intensity; these are assignable to the π→π* transitions, in the region 220—250 nm.[11-14]

The absorption maxima and the intensities of the UV spectra of the above five α-nitro ketones in three solvents are summarized in Table 2. The spectral data are in agreement with the conclusion on the keto–enol equilibria deduced by the ^1H NMR spectroscopy. 2-Nitro-5α-cholestan-3-one **3** and its 4,4-dimethyl derivative **4** in ethanol exhibited intense absorption maxima due to the π→π* transitions of a conjugated nitro group at 343 and 337 nm. The displacement of the absorption maxima to the longer wavelengths, when compared with the absorption maxima of the corresponding nitro olefins, is attributable to the effects of the additional hydroxyl group in the chromophore.

The nitro ketones **3** and **4** also exhibited intense absorption maxima at 310 and 315 nm in hexane respectively although their intensities were reduced in hexane in the case of **3** presumably owing to the presence of a greater amount of the keto form in the nonpolar solvent. 3-Nitro-5α-cholestan-2-one (**11**) exhibited weaker absorption maxima at 330 nm in ethanol and at 312 nm in hexane, assignable to the π→π* transitions. The decreased intensities are apparently due to the greater extent of the keto form. As expected, the intensities of absorptions due to the enol forms of the above three α-nitro ketones enhanced in ethanol containing sodium ethoxide where these α-nitro ketones exist exclusively in their enol forms.

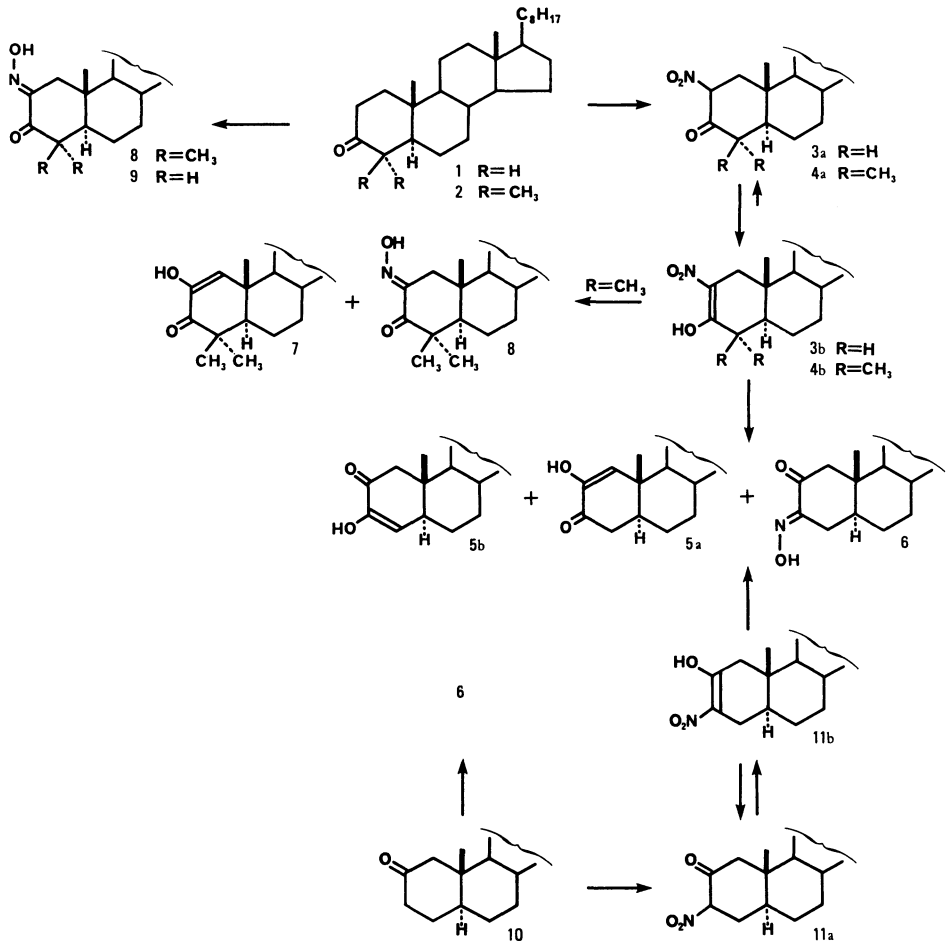
Table 2. UV Spectra of 6-Membered Cyclic α-Nitro Ketones

	λ_{max}/nm (ε)		
	EtOH	Hexane	EtOH-NaOEt
3	343 (14800)	310 (8900)	338 (13800)
4	337 (12300)	315 (10400)	330 (18400)
11	330 (5100)	312 (7700)	338 (14900)
13	345 (60) 284 (110)	270—330 (ca. 400)	342 (450) 235 (9800)
17	239 (1550) 291 (220)	226 (1890) 274 (160)	235 (6500)

6α-Nitro-5α-cholestan-7-one (**17**), on the other hand, exhibited broad weak absorption at 274 nm in hexane. The absorption maximum is assignable to the n→π* transition of the nitro- and/or the carbonyl groups on the basis of a bathochromic shift of the band in ethanol as well as its intensity. This α-nitro ketone **17** was found to be hardly enolizable at room temperature since no appreciable change of the UV spectrum was observed when it was taken in ethanol containing sodium ethoxide.

4β-Nitro-5β-cholestan-3-one (**13**) in hexane exhibited broad and weak absorption maxima from 270 to 330 nm attributable to the n→π* transitions of the nitro and/or the carbonyl group of the keto form as well as the band attributable to the π→π* transition of the conjugated nitro group of the enol form which is present in a trace amount.

Photochemistry of Cyclic α-Nitro Ketones. (a) 2-Nitro-5α-cholestan-3-one (3) (Scheme 1). Photolysis of **3** in ethanol with a Hanovia 450-W high pressure Hg arc through Pyrex for 2.5 h in an atmosphere of nitrogen gave a product mixture from which a crystalline mixture of diosphenols, (22.5%) 2-hydroxy-5α-cholest-1-en-3-one (**5a**) and its isomer **5b**,[15-21] as well as a ketonic product **6** (11.6%) were isolated by means of preparative TLC (Scheme 1). No other pure



Scheme 1.

products were isolated. Recrystallization of the mixture of diosphenols from ethanol gave a mixture of **5a** and **5b**. The ratio of **5a** and **5b** determined before and after recrystallization by ^{1}H NMR spectroscopy was approximately 1:1.

High resolution mass spectrometry indicated that the ketonic product **6** has the molecular formula $C_{27}H_{45}NO_2$. The IR spectrum exhibited a series of bands assignable to a hydroxyimino and an unstrained carbonyl group. The ^{1}H NMR spectrum of **6** exhibited two one-proton doublets at δ 2.77 and 2.09 (J=17.58 Hz) and a doublet of a doublet centered at δ 2.99 (J=19.42 and 5.5 Hz). These spectral results suggested that the structure of **6** was either 5α-cholestane-2,3-dione 2-oxime (**8**)[6,16,22,23] or 5α-cholestane-2,3-dione 3-oxime (**6**). The structure of **6** was determined to be the latter by a direct comparison between oximes **6** and **8** prepared by means of nitrosation of 5α-cholestan-2-one and 5α-cholestan-3-one. The oxime **6** obtained by the photolysis was identical with the oxime prepared by the nitrosation of 5α-cholestan-2-one and differed from the oxime prepared by the nitrosation of 5α-cholestan-3-one. The signals at δ 2.77, 2.09, and 2.99 in the ^{1}H NMR of **6** were then assignable to the 1α-H, 1β-H, and 4α-H respectively. The considerable downfield shift of the signal due to the 4α-H is attributable to the deshielding by the hydroxyl group of the hydroxyimino function and indicates that the hydroxyl of the hydroxyimino group was oriented anti to the 2-carbonyl group.[24] The ^{1}H NMR spectrum of **8** exhibited two doublets at δ 1.93 and 3.22 assignable to the 1α-H and 1β-H. The considerable downfield shift of the signal due to the 1β-H is similarly attributable to the deshielding by the hydroxyimino group, which is oriented anti to the carbonyl group.

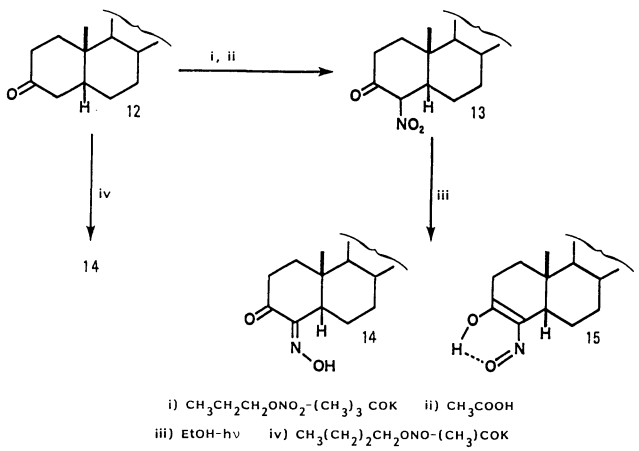
(b) Photolysis of 4,4-Dimethyl-2-nitro-5α-cholestan-3-one (4) (Scheme 1). Photolysis of 4,4-dimethyl derivative **4** was then undertaken. The photolysis of **4** in ethanol for 1 h under the same conditions as for the photolysis of **3b** led to a 76% conversion of the oxime and gave a mixture of the products. Preparative TLC of the products gave a diosphenol, 4,4-dimethyl-2-hydroxy-5α-cholest-1-en-3-one (**7**),[25,26] and ketonic product **8** in 22% and 11.6% yields. The structure of **8** was deduced by means of spectroscopy (see Experimental). High resolution mass spectrometry indicated that the ketonic product **8** had the molecular

formula $C_{29}H_{49}NO_2$. The IR spectrum exhibited bands assignable to a hydroxyimino and an unstrained carbonyl group. The ^1H NMR spectrum indicated two doublets at δ 2.17 and 3.03 (J=18.7 Hz). These spectral results suggested that the structure of the product was 4,4-dimethyl-5α-cholestane-2,3-dione 2-oxime (**8**).[27] This assumed structure was confirmed by a direct comparison with the specimen obtained by the synthesis. The signals at δ 2.81 and 3.02 in the ^1H NMR spectrum are assignable to the 1α-H and 1β-H respectively. Thanks to a considerable shift of the signal of the 1β-H to the low field in comparison with the signal of the 1α-H, it was confirmed that the hydroxyl group in the hydroxyimino group is again oriented anti to the carbonyl group.

(c) Photolysis of 3-Nitro-5α-cholestan-2-one (11). Photolysis of nitro ketone **11** in ethanol with a Eikosha 500-W high pressure Hg arc through a Pyrex for 3 h in an atmosphere of nitrogen resulted in a 93% conversion of the nitro ketone and gave a mixture of products from which we obtained a poor yield of the diosphenols, 5α-cholestane-2,3-dione (**5a** and **5b**)(4%) produced by the photolysis of nitro ketone **3** and a ketonic product **6** (18%). The product **6** had the molecular formula $C_{27}H_{45}NO_2$ and was identical in every respects with 5α-cholestane-2,3-dione 3-oxime (**6**) obtained by the photolysis of 2-nitro-5α-cholestan-3-one (**3**).

(d) Photolysis of 4β-Nitro-5β-cholestan-3-one (13) (Scheme 2). As we have said, nitro ketone **13** exists as its keto form in ethanol while nitro ketones, **3**, **4**, and **11** exist mostly as their enol froms **3b**, **4b**, and **11b** in the solvent. It is, therefore, of considerable interest to know how the difference in the tautomeric nature of the nitro ketones is reflected in the products of their photolysis.

The photolysis of nitro ketones **13** in ethanol for 3 h under the conditions described above resulted in a 51% conversion of the substrate and gave a mixture cf products which was subjected to column chromatography

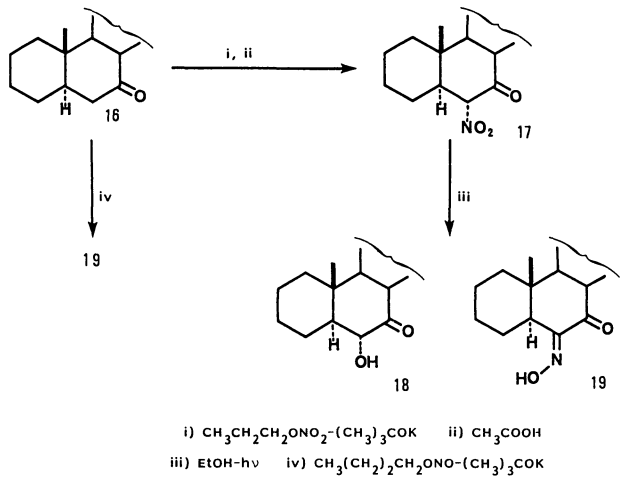


Scheme 2.

to give two crystalline products **14** and **15**. The compound **14** had the molecular formula $C_{27}H_{45}NO_2$ (high resolution mass spectrometry). The IR spectrum exhibited bands at 3340, 1693, and 1571 cm^{-1} assignable to a hydroxyimino group conjugated with a carbonyl group. This result, together with the ^1H NMR spectrum, indicated that it was 5β-cholestane-3,4-dione 4-oxime (**14**). The structure was confirmed by a direct comparison with oxime **14** which was prepared by nitrosation of 5β-cholestan-3-one **12**.

The ^1H NMR spectrum of **14** exhibited a doublet of a doublet at δ 2.93 (1H) with J=5.5 and 2.9 Hz assignable to the angular 5β-H. The observed displacement of this signal to the low field indicates that the 5β-H is deshielded by the hydroxyl of the hydroxyimino function which is oriented anti to the carbonyl group. High resolution mass spectrometry of compouhd **15** indicated that compound **15** is an isomer of α-hydroxyimino ketone **14**. The product had a double melting point and the higher melting point was nearly in agreement with that exhibited by α-hydroxyimino ketone **14**. IR spectrum exhibited a broad band at 3330 cm^{-1} due to a hydrogen-bonded hydroxyl group but no band due to a carbonyl group. Instead, there was a weak band at 1650 cm^{-1} due to a C=C bond in the IR spectrum. These results together with its ^1H NMR spectrum indicated that compound **15** was 4-nitroso-5β-cholest-3-en-3-ol. The assigned structure was then confirmed by isomerizing **15** to the oxime **14**. The nitroso steroid **15** was heated up to 140 °C and recrystallization of the melt gave a specimen which was identical with α-hydroxyimino ketone **14**. So far the nitroso-monomer has rarely been isolated. The nitroso-monomer **15** in this case may perhaps be isolated as a result of stabilization by an intramolecular hydrogen bond between the hydroxyl group and the nitroso oxygen. The mixture of the products of the photolysis was carefully examined by means of TLC but no cyclic α-diketones and cyclic imides were found.

(e) Photolysis of 6α-Nitro-5α-cholestan-7-one (17)[6] (Scheme 3). Nitro ketone **17** is again in a keto form in ethanol as in the case of nitro ketone **13**. Photolysis of nitro ketone **17** in ethanol for 7 h under the conditions as mentioned above, resulted in a 59% conversion and gave a complex mixture of the products. Two crystalline products **18** and **19** were isolated in 13 and 12% yields from the products by means of preparative TLC. The molecular formulae of **18** and **19** were determined to be $C_{27}H_{46}O_2$ and $C_{27}H_{45}NO_2$ by means of high-resolution mass spectrometry. The structure of product **18** was confirmed to be 6α-hydroxy-5α-cholestan-7-one on the basis of their IR and ^1H NMR spectra (see Experimental). The structure of product **19** was also deduced to be 5α-cholestane-6,7-dione 6-oxime on the basis of the IR, ^1H NMR, and mass



Scheme 3.

spectra (see Experimental) and this was finally confirmed by its preparation by nitrosation of 5α-cholestan-7-one (**16**). The ^1H NMR spectrum of **19** exhibited a doublet of a doublet at δ 2.17 (J=11.6 and 2.9 Hz) assignable to the 5α-H and a triplet at δ 2.48 (J=10.8 Hz) assignable to the 8β-H. It should be noted that although the hydroxyl group of the hydroxyimino function is almost certainly oriented anti to the carbonyl group, the 5α-proton is not deshielded to the same extent as 5β-proton of 5β-cholestane-3,4-dione 4-oxime. An inspection of the molecular model indicates that the orientation of the hydroxyl group is unable to deshield the axial 5α-proton. In the ^1H NMR spectrum of **19**, there was another one-proton multiplet centered at δ 2.28 assignable to the 4α-H which is likely to be deshielded by the hydroxyl group.

Discussion

A wide variety of photochemical transformations of aromatic, α,β-unsaturated, and aliphatic nitro compounds have been reported. The subject was first reviewed in 1969[14] and has recently been updated.[28]

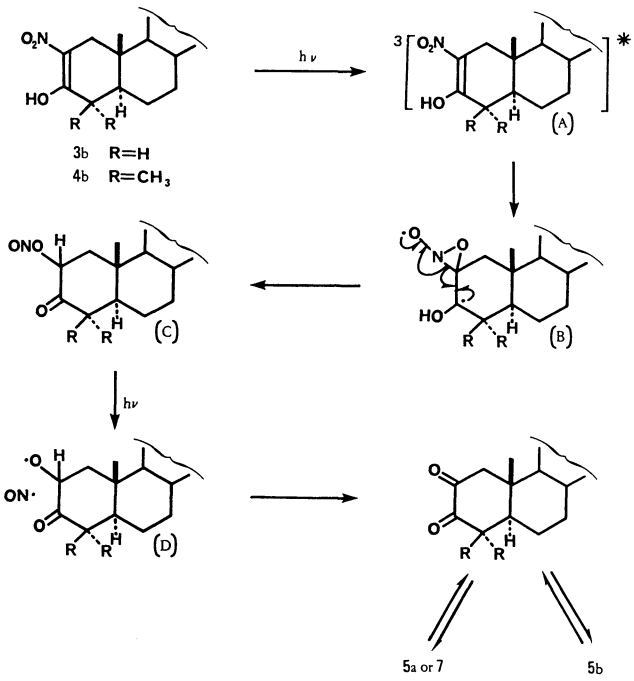
Although the photochemistry of some cyclic α-nitro ketones which exist in their keto form in solution has been investigated by Reid and Tucker,[4] no investigation has been carried out on the photochemistry of cyclic α-nitro ketones which in solution exist predominantly as their enol forms. The cyclic α-nitro ketones which exist as their enol forms are regarded as substituted α,β-unsaturated nitro compounds.

Chapman and his colleagues were the first to report the photochemical transformation of 2-nitro-1-phenylpropane into 1-hydroxyimino-1-phenyl-2-propanone via nitro-nitrite rearrangement.[29] Analogous photorearrangements to hydroxyimino ketones via the Chapman rearrangement have since been reported of several acyclic nitroalkenes, β-bromo-β-nitrostyrene,[30] *cis*-α,4-dinitrostilbene,[31] 1-aryl-2-nitro-1-propenes,[32] 1-(2-pyridyl)- and 1-(3-pyridyl)-2-nitro-1-alkenes,[33] and simple aliphatic nitroalkenes.[34] Intramolecular cycloaddition followed by a carbon–carbon double bond cleavage has been reported[31,32] to compete with the nitro–nitrite rearrangements in some of the above nitroalkenes.

The analogous photochemical formation of α-hydroxyimino ketones with the accompanying formation of cyclic ketones and enones via nitro–nitrite rearrangements have been observed for 6-membered cyclic nitroalkenes.[34,35] Another variation of the reported photochemistry of nitroalkenes is a photoinduced deconjugation which takes place when intramolecular abstraction of γ-hydrogen is possible.[34]

Our experiments have shown that the common products of the photolysis of the 6-membered cyclic α-nitro ketones which exist as their enol forms in protic solvents are cyclic α-diketones and cyclic α-hydroxyimino ketones. It should be noted that no cyclic imides, which have been found in the products of the photolysis of 2-nitrocycloheptanones and α-nitrocamphor,[4] were found in the products of the present photolysis.

The formation of α-diketones **5** and **7** from **3b**, **4b**, and **11b** is analogous to the formation of cyclic ketones in the photolysis of cyclic nitroalkenes. The pathway to these α-diketones involving the nitro–nitrite rearrangement is outlined in Scheme 4. Thus, excited 6-membered cyclic α-nitro ketones (**A**) rearrange to the corresponding cyclic α-hydroxy ketone nitrites (**C**) through oxaziridine intermediate (**B**). Disproportionation or the scission of a hydrogen atom of the alkoxyl



Scheme 4.

radical (**D**) generated from the nitrite (**C**) affords cyclic α-diketones such as **5a**, **5b**, or **7**.

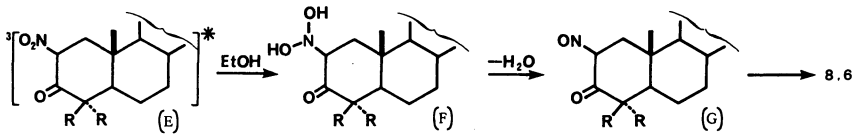
On the other hand, the path of the formation of cyclic α-hydroxyimino ketones from the excited cyclic α-nitro ketones (**4a**→**8**, **11a**→**6**) is outlined in Scheme 5. As outlined, these cyclic α-hydroxyimino ketones are simply derived through the isomerization of α-nitroso ketone (**G**) which can be formed from the intermediate (**F**) generated by the hydrogen abstraction from the solvent by the n,π* triplet excited nitro group[36-39] of the keto form (e.g., **E**) or the enol forms (e.g., **A**).

It is very likely, however, that α-hydroxyimino ketone **6** or **8** from α-nitro ketone **4** or **11** is formed from their keto form since α-hydroxyimino ketone **14** is obtained in the photolysis of α-nitro ketone **13** which exists exclusively in the keto form in ethanol.

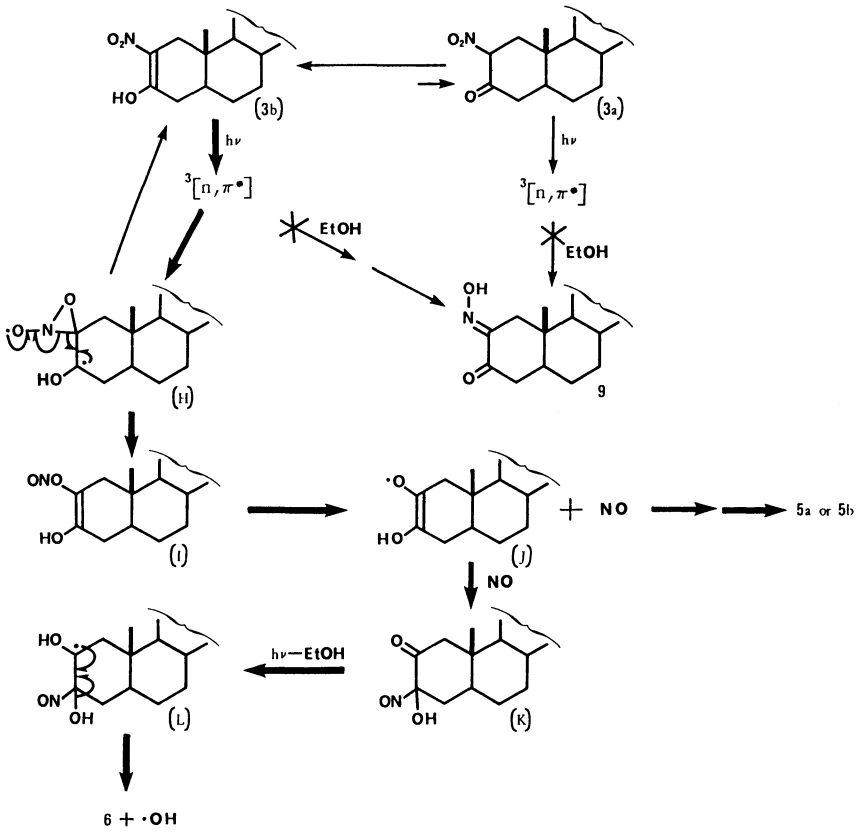
An anomalous result in the present experiments, however, is the formation of 5α-cholestane-2,3-dione 3-oxime (**6**) in the photolysis of 2-nitro-5α-cholestan-3-one (**3a**).

One of the probable geneses of the anomalous formation of α-hydroxyimino ketones **6** from 2-nitro-5α-cholestan-3-one **3** is outlined in Scheme 6. Thus, irradiation of 2-nitro-5α-cholestan-3-one (**3**) generates the n,π* triplet from which the nitrite (**I**) is formed by the Chapman rearrangement.[28-35] The combination of nitrogen monoxide with the C-3 of the enoloxyl radical (**J**) generated from the nitrite may give a nitroso ketone (**K**). The hydrogen abstraction by the excited nitroso ketone (**K**) then may give α-hydroxyimino ketone **6** through the removal of a hydroxyl radical from a ketyl radical (**L**). The competing process from the n,π* triplet, a hydrogen abstraction from the solvent, leading to the formation of α-hydroxyimino ketone **8** is unlikely to be as efficient as the Chapman rearrangement.

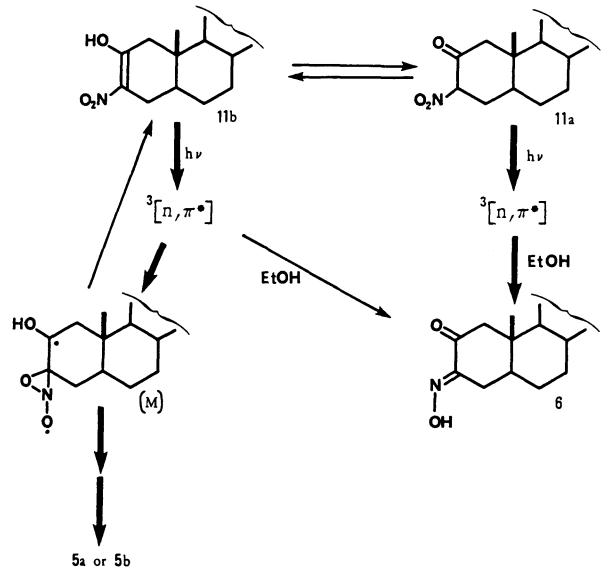
No α-hydroxyimino ketones based on the pathway involving the Chapman rearrangement outlined in Scheme 6 were formed in the photolysis of 3-nitro-5α-cholestan-2-one (**11**) and 4,4-dimethyl-2-nitro-5α-cholestan-3-one (**4**) even though photolysis resulted in the



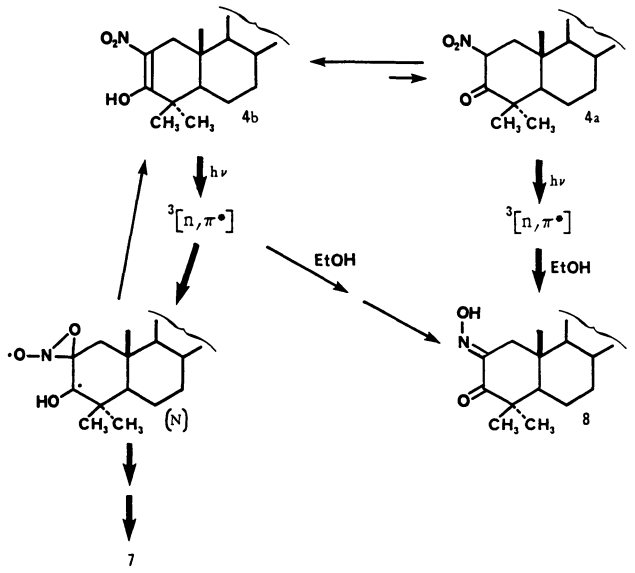
Scheme 5.



Scheme 6.



Scheme 7.



Scheme 8.

formation of diketones **5** or **7**, which involves the nitro-nitrite rearrangement as outlined in Schemes 7 and 8. The absence of α-hydroxyimino ketone **9** in the photolysis of nitro ketone **11** based on the mechanism outlined in Scheme 6 is attributable to steric inhibition of the combination of nitrogen monoxide with the C-2 of the intermediate by the 10β-methyl group. The absence of 4,4-dimethyl-5α-cholestane-2,3-dione 3-oxime in the photolysis of nitro ketone **4** is similarly attributable to the steric inhibition of the combination of nitrogen monoxide with the C-3 of the intermediate such as (**J**) (Scheme 6) by the C-4 *gem*-dimethyl group.

There are precedents for the formation of α-hydroxyimino ketones **14** and **19** in the photolysis of α-nitro ketones **13** and **17**, which exist in their keto forms.[4] These products are apparently formed by the elimination of the element of water from the intermediate formed from the hydrogen abstraction from the solvent by the n,π* excited nitro group. The unprecedented isolation of the unstable nitroso intermediate **15** in the photolysis of α-nitro ketone **13** is of interest in connection with this pathway.

The α-hydroxy ketone **18** is likely to be generated from the corresponding nitrite. The nitrite in this case may be formed either through the Chapman rearrangement of the enol form, which exists in a trace amount, or through the dissociation-recombination mechanism[3] of the nitro group of the keto form.[40]

Experimental

Mp's were recorded with a Yanagimoto micro mp apparatus. IR spectra were determined for Nujol mulls with a Hitachi Model 285 infrared spectrophotometer or a JASCO IR 810 infrared spectrophotometer unless otherwise indicated. ^{1}H NMR spectra were determined with a JEOL PS 200 high resolution FT-NMR spectrometer (200 MHz) or a JEOL JNM-FX 270 spectrometer (270 MHz) (solvent, $CDCl_3$; $SiMe_4$ as an internal standard) (Faculty of Pharmaceutical Sciences of this University). TLC was carried out on a Merck Kiesel gel 60-PF_{254}. The high and low resolution mass spectra were determined with a JEOL JMS-D-300 spectrometer (70 eV) (Faculty of Pharmaceutical Sciences of this University). Elemental analyses were performed by the staff of the analytical laboratory of Faculty of Pharmaceutical Sciences.

2-Nitro-5α-cholestan-3-one (2-Nitro-5α-cholest-2-en-3-ol) (3). 5α-Cholestan-3-one (**1**) (2 g 5.18 mmol) was dissolved in *t*-butyl alcohol (50 ml) containing potassium *t*-butoxide (1.5 g, 13.4 mmol). To this solution at 22 °C propyl nitrate (1.5 ml, 15 mmol) was added and the solution was stirred for 2 h at room temperature. The solution was then poured into iced water (200 ml). A yellow-colored potassium salt of α-nitro compound **3** (2.512 g) was collected by filtration. The potassium salt was dissolved in glacial acetic acid (100 ml) by heating. The solution was cooled to room temperature and water was added to the solution to yield colorless crystals of 2-nitro-5α-cholestan-3-one (**3**) (2.157 g, 96.6%), mp 117—125 °C. This nitro ketone was recrystallized from ethanol to yield analytical specimen (1.487 g, 66.6%), mp 132—135 °C (lit,[5] mp 135—136 °C). IR (Nujol) 1616 (C=C), 1513 (conjugated NO_2) 1746, (very weak band, C=O), and 1561 cm^{-1} (very weak bond non-conjugated NO_2); ^{1}H NMR (100 MHz) δ=0.67 (3H, s, 18-H), 0.83 (3H, s, 19-H), and 2.70 (1H, *J*=15.9 Hz, 1-H); MS, *m/z* (rel intensity) 431 (M^+, 83.8%), 227 (64.8, M^+—D-ring) 276 (89.7), 95 (64.0), 81 (65.4), 69 (61.8), 57 (67.4), 55 (94.4), and 43 (100).

4,4-Dimethyl-2-nitro-5α-cholestan-3-one (4). 4,4-Dimethyl-5α-cholestan-3-one (**2**) (5 g) was dissolved in *t*-butyl alcohol (185 ml) containing potassium *t*-butoxide (7.5 g). To this solution, propyl nitrate (5.15 ml) was added and the solution was stirred for 3 h 45 min at room temperature. The solution was then poured into iced water (700 ml). A yellow-colored potassium salt of α-nitro compound (7.4 g) was collected by filtration. The potassium salt was dissolved in glacial acetic acid (200 ml), and water was slowly added to

the solution to yield colorless crystals of 4,4-dimethyl-2-nitro-5α-cholestan-3-one (**4**) (4.2 g, 75.6%). This nitro ketone was recrystallized from hexane to yield an analytical specimen (3.0 g, 54%), mp 123—127 °C. Found: C, 75.74; H, 10.95; N, 2.95%. Calcd for $C_{29}H_{49}NO_3$; C, 75.77; H, 10.74; N, 3.05%. IR (Nujol) 1605 (C=C), 1513 (conjugated NO_2), and 1297 cm^{-1}; ^1H NMR (270 MHz) δ=0.66 (3H, s, 18-H), 0.88 (3H, s, 19-H), 1.30 and 1.32 (each 3H, each s, 4-Me), 2.05 and 2.80 (each 1H, each d, J=15.38 Hz, 1α-H and 1β-H). MS, m/z (rel intensity) 459 (M^+, 100%), 441 (15.3), 412 (M^+-HNO_2, 15.0), 403 (29.2), 315 (58.0), 304 (59.6), 95 (80.8), 81 (70.7), 69 (70.7), 55 (74.1), and 43 (79.1).

3-Nitro-5α-cholestan-2-one (11). 5α-Cholestan-2-one (**10**) (1.5 g) was dissolved in THF (50 ml) containing potassium t-butoxide (1.4 g). To this solution, isopentyl nitrate (2 g) in THF (3 ml) was added over the course of 20 min, while being cooled with Dry Ice–methanol. After the solution was stirred for 40 min at room temperature, the solution was neutralized by the addition of glacial acetic acid. The solution was then poured into water (250 ml) and the solution was extracted with dichloromethane. Combined organic layers were worked up by the usual method. The crude oily nitro ketone (1.786 g) was recrystallized from ethanol to yield crystals of nitro ketone **11** (1.372 g. 81.7%), mp 117—120 °C, ^1H NMR (270 MHz) δ=0.67 (3H, s, 18-H), 0.85 (3H, s, 19-H), 5.28 (0.37H, dd, J=12.9 and 6.9 Hz, 3β-H of the keto form **11b**) and 13.8 (0.63H, s, OH); IR (Nujol) 1735 (C=O), 1619 (C=C), 1562 (non-conjugated NO_2), 1509 cm^{-1} (conjugated NO_2); MS (70 eV), m/z (rel intensity) 431 (M^+, 91.4%), 416 (6.9), 291 (11.3), 276 (M^+—D-ring, 100), 262 (27.9), and 55 (43.3). Found: C, 74.99; H, 10.45; N, 3.09%. Calcd for $C_{27}H_{45}NO_3$: C, 75.13; H. 10.50; N, 3.25%.

4β-Nitro-5β-cholestan-3-one (13). 5β-Cholestan-3-one (**12**) (500 mg, 1.30 mmol) was dissolved in t-butyl alcohol (10 ml) containing potassium t-butoxide (200 mg, 1.79 mmol). To this solution at 22 °C, propyl nitrate (0.15 ml, 1.5 mmol) was added and the solution was stirred for 2.5 h at room temperature. The solution was then poured into iced water (70 ml). Glacial acetic acid was added to this aqueous pale yellow solution of the potassium salt of α-nitro ketone until pH 3. The solution was stirred for 30 min and extracted with dichloromethane. The organic layer was washed with water and dried over anhydrous Na_2SO_4. The workup in the usual way gave an oil (546 mg). This oily 4β-nitro-5β-cholestan-3-one (**13**) crystallized upon the addition of ethanol. (123 mg, 22%), mp 157—160 °C. The filtrate contained the starting 3-ketone and 2,4-dinitro ketone. Found: C, 75.02; H, 10.39; N, 3.27%. Calcd for $C_{27}H_{45}NO_3$: C, 75.13; H, 10.51; N, 3.25%. IR (Nujol) 1714 (C=O), 1558 cm^{-1} (NO_2); ^1H NMR (200 MHz) δ=0.69 (3H, s, 18-H), 1.13 (3H, s, 19-H), and 5.67 (1H, d, J=12.7 Hz, 4α-H); MS, m/z (rel intensity) 431 (M^+, 34.8%), 385 (M^+-NO_2, 30.7), 276 (22.3), 231 (30.7), 229 (37.2), 140 (38.8), 95 (72.4), 81 (75.1), 69 (69.7), 55 (100), and 43 (84.1).

6α-Nitro-5α-cholestan-7-one (17). The α-nitro ketone **17** was prepared according to the procedure reported by Meakins et al.[6] Yield was 34%. Mp 143—144 °C (lit,[6] mp 137—139 °C). IR (Nujol) 1728 (C=O) and 1558 cm^{-1} (non-conjugated NO_2).

Photolysis of 2-Nitro-5α-cholestan-3-one (3). 2-Nitro-5α-cholestan-3-one (**3**) (300 mg, 10.7 mmol) in absolute ethanol (450 ml) was irradiated with a Pyrex-filtered light (Hanovia 450-W high pressure Hg arc) for 1.5 h in an atmosphere of dry nitrogen. The removal of the solvent under a reduced pressure gave an oily residue (341 mg) which was subjected to preparative TLC with benzene to yield two fractions. The more mobile oily fraction (63 mg, 22.5%) was 5α-cholestane-2,3-dione (**5**). Its NMR spectrum indicated that it was a 1:1 mixture of two isomeric enols **5a** and **5b**. Recrystallization of the mixture with ethanol gave a crystalline mixture of 2-hydroxy-5α-cholest-1-en-3-one (**5a**) and its isomer **5b** in a 1 to 1 ratio. Mp 119—155 °C (lit,[21] mp of pure enol **5a**, 163—167 °C). ^1H NMR δ=0.56 (s, 18-H of **5b**), 0.68 (s, 18-H of **5a**), 5.70 (d, J=2.6Hz, 4-H of **5b**), 5.68 (s, OH of **5a** and **5b**), 6.38 (s, 1H of **5a**). The polar fraction (190 ml) was subjected to preparative TLC with a 3:1 benzene–ethyl acetate to yield 5α-cholestan-2,3-dione 3-oxime (**6**) (34 mg, 11.6%). An analytical specimen was obtained by recrystallization with ethanol. Mp 196—198 °C. IR (Nujol) 3628, 3445, and 3228 (OH), 1708, and 1687 (C=O), 1608 and 1585 (C=N), 1272, 1031, and 985 cm^{-1}; ^1H NMR (270 MHz), δ=0.66 (3H, s, 18-H), 0.85 (3H, s, 19-H), 2.77 (1H, d, J=17.6 Hz, 1β-H), 2.09 (1H, d, J=17.2 Hz, 1α-H), and 2.99 (1H, dd, J=19.4 and 5.5 Hz, 4α-H); EIMS (rel intensity) 415 (M^+, 100%), 400 (6.3), 399 (6.3), 398 (9.5), 261 (28.3), 260 (55.6), and 43 (95.8). Found: m/z 415.3480. Calcd for $C_{27}H_{45}NO_2$: M, 415.3450.

Synthesis of 5α-Cholestan-2,3-dione 3-Oxime (6). To a solution of the ketone (100 mg) in t-butyl alcohol (10 ml) containing potassium t-butoxide (35 ml), butyl nitrite (0.035 ml) was added and the solution was stirred for 30 min at room temperature. The solution was then poured into iced water. After aq. 2 M hydrochloric acid (1 M=1 mol dm^{-3}) had been added, the solution was extracted with diethyl ether. The combined organic layers were washed with water and dried over anhydrous sodium sulfate. The usual workup of the solution gave an oily product (193 mg) which was subjected to preparative TLC with a 2:1 benzene–ethyl acetate to give a crude oxime (83 mg, 77%). Recrystallizations from ethyl acetate–methanol gave pure oxime **6**, (54 mg), mp 196—198 °C. This oxime was identical with oxime **6** obtained from the photolysis of nitro ketone **3**.

Synthesis of 5α-Cholestane-2,3-dione 2-Oxime (9),[6,16,22,23] This hydroxyimino ketone **9** was prepared according to the procedure reported by Chadwick et al.[6] Butyl nitrite was used instead of pentyl nitrite. The oxime which was recrystallized from THF melted at 271—274 °C. (lit, mp 240—242 °C;[6] 203—205 °C;[16] 268—270 °C[22,23]). IR (Nujol) 3136 (OH), 1718 (C=O), 1619 (C=N), 1294, 975, and 817 cm^{-1}; MS, m/z (rel intensity) 415 (M^+, 79.8%), 398 [$(M-OH)^+$, 100], 384 (27.9), 314 (20.7), 260 (76.3), 244 (27.1), 216 (22.3), 136 (36.3), 121 (39.1), 107 (37.0), 95 (55.8), 81 (55.1), 69 (52.4), 55 (73.8), and 43 (66.7%); ^1H NMR (270 MHz) δ=0.67 (3H, s, 18-H), 0.85 (3H, s, 19-H), 1.93 (1H, d, J=18.0 Hz, 1α-H), 2.44 (1H, dd, J=5.5 and 18.9 Hz, 4-H), and 3.22 (1H, d, J=18.0 Hz, 1β-H).

Photolysis of 4,4-Dimethyl-2-nitro-5α-cholestan-3-one (4). 2-Nitro steroid (**4**) (350 mg, 0.76 mmol) in absolute ethanol (350 ml) was flashed with nitrogen and was irradiated with a Pyrex-filtered light (Eikosha 500-W high pressure Hg arc) for 1 h in an atmosphere of dry nitrogen. The removal of the solvent under a reduced pressure gave an oily residue (352 mg) which was subjected to preparative TLC with chloroform to yield three fractions. The most mobile fraction (83 mg, 24%) was the starting material (**4**). The second mobile fraction (54 mg, 21.6%) was 4,4-dimethyl-2-hydroxy-5α-cholest-1-en-3-one (**7**) which was recrystallized

from ethanol–water to yield crystals, mp 165—169 °C (lit, mp 165—167 °C,[25] 168 °C[26]). IR (Nujol) 3442, 3412 (OH), 1668, and 1652 cm^{-1} (C=C and C=O of diosphenol); EIMS, *m/z* (rel intensity) 428 (M^+, 67.2%), 425 [$(M-Me)^+$, 25.4]. 400 [$(M-CO)^+$, 16.3], 385 (14.9), 341 (13.1), 315 (37.1), 300 (37.5), 247 (22.8), 166 (28.8), 81 (54.6), 69 (55.1), 55 (64.5), and 43 (100); ^1H NMR (270 MHz) δ=0.68 (3H, s, 18-H), 1.11 (3H, s, 19-H), 1.13 (3H, s, 4β-Me), 1.91 (3H, s, 4α-Me), 5.99 (1H, s, OH), and 6.40 (1H, s, 1-H). The most polar fraction (33 mg, 12.7%) was 4,4-dimethyl-5α-cholestane-2,3-dione 2-oxime (**8**)[27] which was recrystallized from ethanol–water. Mp 202—205 °C (lit,[27] mp 197—198 °C). IR (Nujol), 3270 (OH), 1705 (C=O), 1612 (C=N), 962, and 759 cm^{-1}; ^1H NMR (270 MHz) δ=0.66 (3H, s, 18-Me), 0.85 (3H, s, 19-Me), 1.12 (3H, s, 4β-Me), 1.17 (3H, s, 4α-Me), 2.17 (1H, d, *J*=18.7 Hz, 1α-H), and 3.03 (1H, d *J*=18.7 Hz, 1β-H).

Synthesis of 4,4-Dimethyl-5α-cholestane-2,3-dione 2-Oxime (8). This oxime was prepared according to the procedure reported by French workers.[27] Mp 202—205 °C (lit,[27] mp 197—198 °C). This hydroxyimino ketone was identical with the specimen obtained by the photolysis of 4,4-dimethyl-2-nitro-5α-cholestan-3-one.

Photolysis of 3-Nitro-5α-cholestan-2-one (11). 3-Nitro-5α-cholestan-2-one (**11**) (300 mg, 0.7 mmol) in ethanol (300 ml) was irradiated with a Pyrex-filtered light (Eikosha 500-W high pressure Hg arc) for 3 h in an atmosphere of a nitrogen. A workup of the irradiated solution as in the case of 2-nitro steroid **3b** gave an oily residue (323 mg) which was subjected to preparative TLC with dichloromethane to yield three fractions. The most mobile fraction (22 mg, 7.5%) was the starting material **11b**. The second mobile fraction (11 mg, 4.2%) was a mixture of α-diketones **5a** and **5b** and it was recrystallized from methanol–water to yield a mixture of α-diketones **5a** and **5b** mp 116—158 °C. The most polar fraction (47 mg, 17.7%) was 5α-cholestane-2,3-dione 3-oxime (**6**) which was recrystallized from methanol–water. Mp 196—198 °C. This oxime was identical with the specimen obtained by the photolysis of 2-nitro-5α-cholestan-3-one (**3a**).

Photolysis of 4β-Nitro-5β-cholestan-3-one (13). Nitro steroid **13** (300 mg, 0.7 mmol) in absolute ethanol (400 ml) in a quartz vessel was irradiated with a low pressure Hg arc in a Rayonet chamber reactor for 3 h in an atmosphere of dry nitrogen. The removal of the solvent under reduced pressure gave an oily residue (330 mg) which was subjected to the separation by means of column chromatography (silica gel). Elution with benzene gave the starting nitro steroid (148 mg) and then nitroso steroid **15** (37 mg, 25.2%). The latter was recrystallized from ethanol to yield a specimen for analysis, mp 113—119 °C and 167—174 °C. IR (Nujol) 1650 (C=C), 1528 and 1000 cm^{-1}; ^1H NMR (200 MHz) δ=0.67 (3H, s, 18-H), 1.14 (3H, s, 19-H); EIMS *m/z* (rel intensity) 415 (M^+, 14.2%), 398 [$(M-OH)^+$, 43.1], 356 (21.9), 140 (39.7), and 124 (100). Found: *m/z* 415.3457. Calcd for $C_{27}H_{45}NO_2$: M, 415.3450. Elution with a 99:1 diethyl ether–methanol gave a crude α-keto oxime **14** (74 mg, 50.4%) which was subjected to preparative TLC with a 97:3 dichloromethane–methanol to yield 30 mg of α-keto oxime **14**. It was recrystallized from ethanol to yield an analytical specimen, mp 186—188 °C. IR (Nujol) 3340 (OH), 1693 (C=O), and 1571 cm^{-1} (C=N); ^1H NMR (270 MHz), δ=0.66 (3H, s, 18-H) and 1.09 (3H, s, 19-H), 2.93 (1H, dd, *J*=5.5 and 2.9 Hz, 5β-H), and 2.47 (2H, m, 2-H);MS, *m/z* (rel intensity) 415 (M^+, 9.4%), 398 [$(M-OH)^+$, 33.0], 356 (24.5), 276 (14.0), 260 (100), 160 (6.5), 128 (31.2), 124 (86.8), 109 (31.4), 95 (38.5), 81 (41.6), 69 (40.5), 55 (52.0), and 41 (44.7); Found: *m/z* 415.3440. Calcd for $C_{27}H_{45}NO_2$: M, 415.3448.

Synthesis of 5α-Cholestane-3,4-dione 4-Oxime (14). To 5β-cholestan-3-one (100 mg) in *t*-butyl alcohol (10 mg) containing potassium *t*-butoxide (35 ml), butyl nitrite (0.035 ml) was added. The solution was stirred for half an hour at room temperature and poured into iced water. After aq. 2 M hydrochloric acid had been added, the aq. solution was extracted with diethyl ether. The combined ethereal extracts were washed with water and dried over anhydrous sodium sulfate. The usual work-up of the solution gave an oily hydroxyimino ketone (141 mg). This crude product was subjected to preparative TLC with a 2:1 benzene–ethyl acetate to give a crude oxime (66 mg, 66%). The specimen for analysis (27 mg) was obtained by recrystallizing from methanol–water. It was identical with oxime **14** obtained by the photolysis of 4β-nitro-5β-cholestan-3-one (**13**). Mp 186—188 °C.

Photolysis of 6α-Nitro-5α-cholestan-7-one (17). 6α-Nitro-5α-cholestan-7-one (**17**)(300 mg, 0.7 mmol) in ethanol (300 ml) was irradiated with a Pyrex-filtered light (Eikosha 500-W high pressure Hg arc) for 7 h in an atmosphere of a nitrogen. Evaporation of the solvent under a reduced pressure gave an oily residue (315 mg) which was subjected to preparative TLC with dichloromethane to yield three fractions. The most mobile fraction (122 mg, 40.6%) was the starting material. The second mobile fraction (27 mg, 13.2%) was 6α-hydroxy-5α-cholestan-7-one (**18**). The ketone **18** was recrystallized from ethanol–water to yield the specimen for analysis. Mp 123—128 °C. IR (Nujol) 3468 (OH) and 1705 cm^{-1} (C=O); ^1H NMR (270 MHz) δ=0.67 (3H, s, 18-H) 1.11 (3H, s, 19-H), 2.44 (1H, br. t, *J*=11.7 Hz, 8β-H), 3.15 (1H, d, *J*=4.5 Hz, OH), and 3.86 (1H, ddd, *J*=11.82, 4.5 and 1.1 Hz, 6β-H); ($CDCl_3$–D_2O) δ=3.86 (1H, dd, *J*=11.72 and 1.1 Hz, 6β-H); MS *m/z* (rel intensity) 402 (M^+, 100%), 384 [$(M-H_2O)^+$, 23], 271 (13.4), 257 (13.5), 247 (16.3), 231 (15.7), 194 (24.9), 125 (45.9), 109 (37.8), 95 (47.3), 81 (52), 55 (60.6), and 43 (55.8); Found: *m/z* 402.3517. Calcd for $C_{27}H_{46}O_2$: M, 402.3498.

The most polar fraction (25 mg, 12.2%) was 5α-cholestane-6,7-dione 6-oxime (**19**) and this was recrystallized from methanol–water to give an analytical specimen. Mp 155—158 °C. IR (Nujol) 3292 cm^{-1} (OH), 1717 (C=O), and 1673 (w, C≡N): ^1H NMR (270 MHz) δ=0.67 (3H, s, 18-H), 0.98 (3H, s, 19-H), 2.17 (1H, dd, *J*=11.72 and 2.94 Hz, 5α-H), 2.49 (1H, t, *J*=11.0 Hz, 8β-H) and 8.76 (1H, s, NOH); MS *m/z* (rel intensity) 415 (M^+, 43.6%), 398 [$(OH)^+$, 43.0%)], 370 (73.0), 344 (100), 95 (90.4), 81 (68.3), 69 (84.5); Found: *m/z* 415.3443; Calcd for $C_{23}H_{45}NO_2$: M, 415.3449.

As in the case of the photoreaction of nitro ketone **13** the absence of cyclic α-diketone and cyclic imides in the products was confirmed by means of TLC and a color reaction ($FeCl_3$–water).

Synthesis of 5α-Cholestane-6,7-dione 6-Oxime (19). To 5α-cholestan-7-one (500 mg) in *t*-butyl alcohol (20 ml) containing potassium *t*-butoxide (500 mg), butyl nitrite (1.8 ml) was added. The solution was stirred for 12 h at room temperature and poured into iced water. After aq. 2 M-hydrochloric acid had been added the aq. solution was extracted with diethyl ether, washed with water and dried over anhydrous sodium sulfate. The usual workup gave an

oily oxime (647 mg) which was subjected to preparative TLC to give a crude keto oxime **19** (97 mg). The oxime was recrystallized from methanol to give the specimen for analysis (40 mg). Mp 155—158 °C. This oxime was identical in every respect with the specimen obtained by the photolysis of nitro ketone **17**.

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40) The nitro–nitrite rearrangement of nitro ketone **13** through a homolytic dissociation-recombination of the nitro group may give rise to 6β-hydroxy-5α-cholestan-7-one nitrite[3] which leads to 6β-hydroxy-5α-cholestan-7-one. The 6β-hydroxy-7-one, however, may readily isomerize to the 6α-isomer **18** through its enol form.