

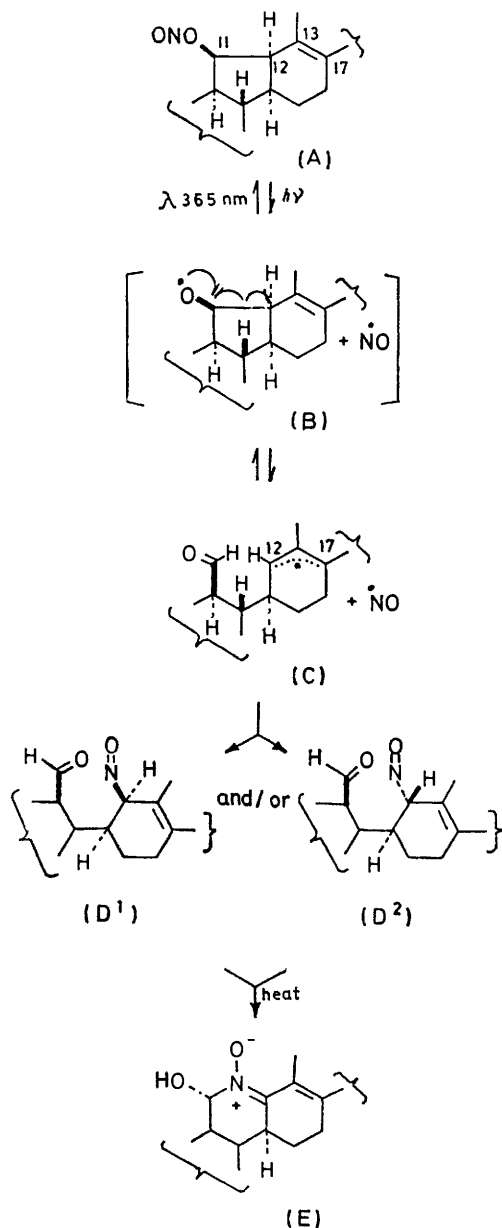
Photoinduced Transformations. Part 32.¹ Scrambling of Unlabelled and [¹⁵N]Nitrogen Monoxide in the Photo-induced Rearrangement of (22S,25S)-5 α -Veratr-13(17)-enin-11 β -yl Nitrites to Nitrones²

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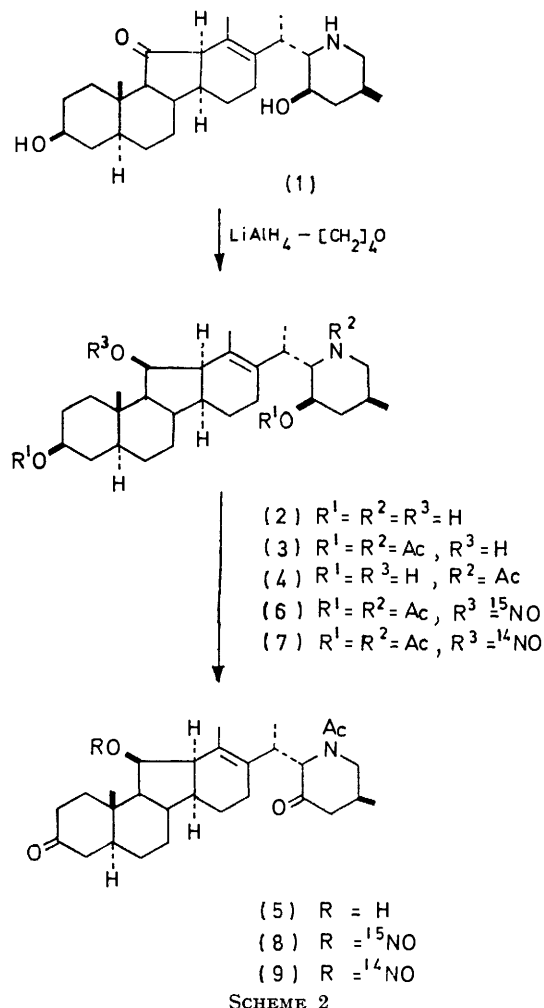
Cross-over experiments with unlabelled nitrite and ¹⁵N-labelled species in the photorearrangement of (22S,25S)-veratr-13(17)-enin-11 β -yl nitrites to the corresponding six-membered ring nitrones indicate that nitrogen monoxide generated from the nitrites in toluene or methanol is randomly distributed in the nitrones. A study of the nitrones obtained by irradiation of each of the two nitrites recovered from the cross-over experiment shows that no scrambling of ¹⁴NO and ¹⁵NO in the nitrites had occurred in the original photolysis. The results imply that a discrete allyl radical intermediate is involved in the reaction, and the observed scrambling between ¹⁵NO and ¹⁴NO takes place after collapse of the 11 β -oxyl radical.

We have shown³ that the excitation of (22S,25S)-5 α -veratr-13(17)-enin-11 β -yl nitrites [partial formula(A)] in

toluene with Pyrex-filtered light induces the formation of a single nitrone [partial structure (E)]. Our subsequent studies confirmed that these cyclic nitrones



SCHEME 1



were formed by irradiation with 365 nm monochromatic light in aprotic or protic medium *via* thermal cyclization

¹ Part 31, H. Suginome, N. Maeda, and T. Masamune, *J.C.S. Perkin I*, 1976, 1312.

² Preliminary report, H. Suginome, T. Mizuguchi, and T. Masamune, *Tetrahedron Letters*, 1971, 4723.

³ H. Suginome, N. Sato, and T. Masamune, *Tetrahedron Letters*, 1969, 3353; *Tetrahedron*, 1971, 27, 4863.

of intermediary nitroso-aldehydes [partial structure (D¹) and/or (D²)] produced by a cleavage of the C(11)-C(12) bond of the oxyl radicals [partial structure (B)] followed by attachment of NO at C-12 (Scheme 1).⁴ It remained to be shown whether or not the rearrangement into the nitroso-aldehydes (D¹) and/or (D²) involved a discrete allyl radical intermediate (C), and, if this was the case, whether the migration of NO generated by homolysis of the O-NO bond of (A) into the C-12 position

peak at *m/e* 558 (0.4%), the steroidal fragment at *m/e* 358 (1.2%), the heterocyclic fragment at *m/e* 198 (98.6%), and peaks at *m/e* 156 (100%) and 114 (13.9%), as usually encountered in this system.³ The dione (5) also shows the usual fragment ions at *m/e* 315 (5%), 297 (13%), and 112 (16%) besides the *M*⁺ peak at *m/e* 419 (2%), but in addition yields significant fragment ions at *m/e* 155 (100%) and 113 (22%), assignable to the fragments *A* and *B* due to McLafferty rearrangement.³

TABLE I
¹H Chemical shifts and coupling constants

Compd.	3 α -H	11 α -H	12 α -H	18-H	19-H	20 β -H	21-H	22 β -H	23 α -H	26-H	27-H	NAc, OAc
(3)	5.32br	5.86 (q)	7.35 (q)	8.27 (s)	9.03 (s)	6.86 (q)	8.87 (d)	5.22 (d)	4.90br (s)	8.87 (d)		7.97 (s), 7.94 (s)
(4)	6.41	5.86 (q) ^b	7.35 (q)	8.24 (s)	9.03 (s)	6.91 (q)	8.89 or 8.80 (d)	5.27br (d)	5.86br (s)	8.89 or 8.80 (d)	<i>a</i>	7.88 (s)
(5)		5.79 (q)	<i>a</i>	8.26 (s)	8.85 (s)	6.71 (q)	8.99 or 9.06 (d)	5.01 (d)		8.99 or 9.06 (d)	6.43br (s)	7.94 (s)
(7)	5.34	3.81 (q)	<i>a</i>	8.42 (s)	9.34 (s)	<i>a</i>	8.94 or 8.89 (d)	5.28 (d)	4.99br (s)	8.94 or 8.89 (d)		7.90 (s), 7.98 (s)
(8)		3.75 (q)	<i>a</i>	8.40 (s)	9.16 (s)	<i>a</i>	9.00 or 9.06 (d)	5.00 (d)		9.00 or 9.06 (d)	<i>a</i>	7.89 (s)
Nitrone A (¹⁴ N)	<i>ca.</i> 5.34	<i>ca.</i> 5.34 (d)		7.93 (s)	9.09 (s)	6.84 (s)	8.88 (d)	5.22 (d)	4.97br (s)	8.88 (d)	6.68br (s)	7.98 (s), 8.01 (s)
Nitrone A (in pyridine)		5.18 (d)		7.71 (s)	9.24 (s)	<i>a</i>	8.89 or 8.94 (d)	4.96 (d)	4.91br (s)	8.88 or 8.94 (d)	6.71br (s)	8.96 (s), 8.05 (s), 8.07 (s)
Nitrone B (¹⁴ N)		5.12br (d) (11 β -H)	<i>a</i>	7.85 (s)	8.88 (s)	6.63 (q)	8.97 or 9.04 (d)	4.97 (d)		8.97 or 9.04 (d)	<i>a</i>	7.90 (s)
Compd.		11 α -H 12 α -H	11 α -H (11 β -H), 9 α -H	12 α -H, 14 α -H	20 β -H, 21-H	20 β -H, 22 β -H	22 β -H, 23 α -H	25 α -H, 26-H				
(3)		5.3	2.7	9.8	6.6	10.5	1.5	6.6				
(4)		5.4	<i>a</i>	9.8	6.6 or 7.2	11.1	1.5	6.6 or 7.2				
(5)					6.0 or 6.6	10.5		6.0 or 6.6				
(7)		5.7	3.0	<i>a</i>	6.6	10.5	1.5	6.6				
(8)				<i>a</i>	5.4 or 6.6	10.8		5.4 or 6.6				
Nitrone A(¹⁴ N)			<i>a</i>		6.6	10.5	1.5	6.6				
Nitrone A (in pyridine)			11 β -H, 9 α -H	7.5	<i>ca.</i> 6	10.5	1.5	<i>ca.</i> 6				
Nitrone B(¹⁴ N)			5.21		6.0 or 6.6	11.1		6.0 or 6.6				

^a Definite chemical shifts could not be obtained. ^b Coincided with 23 α -H signal.

of the nitroso-aldehyde (D¹) and/or (D²) took place in an intermolecular or an intramolecular manner. We now report the details of our investigations which clarify these points.²

Synthesis and Irradiation of Unlabelled and [¹⁵N]Nitrites.—The two new (22*S*,25*S*)-5 α -veratr-13(17)-en-11 β -ols (3) and (5) were prepared from the known (22*S*,25*S*)-3 β ,23 β -dihydroxy-5 α -veratr-13(17)-en-11-one (1)⁵ (Scheme 2). Thus, the diol (1) was reduced with lithium aluminium hydride in boiling tetrahydrofuran to the corresponding 11 β -ol (2) in 59% yield. Partial acetylation of the 11 β -ol (2) at room temperature afforded the *N*-acetyl 3,23-diacetate (3) in 69% yield, hydrolysis of which yielded the triol (4). Sarett oxidation afforded (22*S*,25*S*)-*N*-acetyl-11 β -hydroxy-5 α -veratr-13(17)-en-2,23-dione (5) in 26% yield. The electron impact mass spectra of the *N*-acetyl diacetate (3) and the 2,23-dione (5) show different modes of fragmentation.³ Compound (3) shows an *M*⁺ + 1

* In our preliminary communication² this fragment ion was mistakenly described as a base peak. The reported² ratio of intensities between *m/e* 324 and 325 is slightly different from that given here.

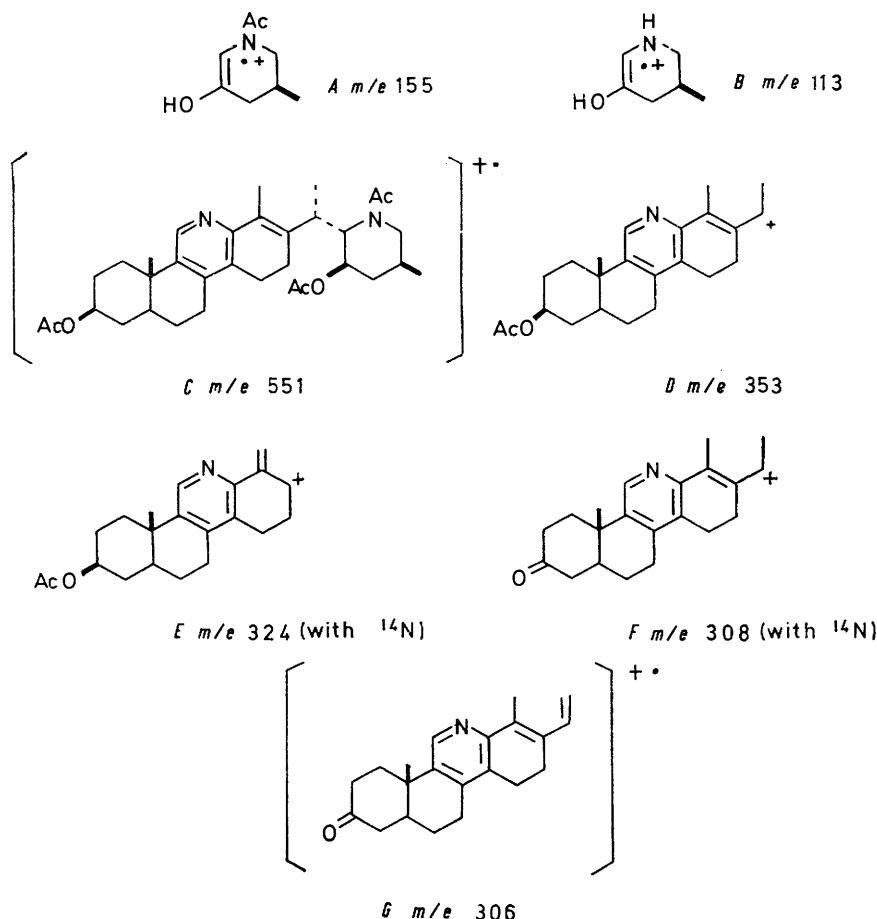
The two 11 β -ols (3) and (5) were nitrosated with unlabelled or sodium [¹⁵N]nitrite in hot acetic acid, or with nitrosyl chloride in pyridine to afford the two nitrites (6) and (8) (designated AN-15 and BN-15) labelled with ¹⁵N in the nitrite moieties and the two unlabelled nitrites (7) and (9) (designated AN-14 and BN-14). Irradiation of the nitrite AN-14 (7) in toluene with Pyrex-filtered light (100 W Hg arc) under argon led to a nitrone A (with ¹⁴N) as virtually the sole product, as in the previous case.³ Under the same conditions the nitrite BN-14 (9) afforded a nitrone B (with ¹⁴N) in 33% yield. The assignments of the n.m.r. signals of the nitrones A and B are in Table I.

The electron impact mass spectrum of the nitrone A showed no molecular ion, and revealed a series of peaks at *m/e* 551 (1.4%), 353 (8.9%), and 325/324 (6.7/30.4%),* 198 (28.6%), 156 (100%), and 114 (28.6%). The former three were assignable to the fragment ions *C*, *D*, and *E*, respectively and the latter three to the usual hetero-

⁴ H. Sugimoto, T. Mizuguchi, and T. Masamune, *J.C.S. Chem. Comm.*, 1972, 376.

⁵ T. Masamune, M. Takasugi, M. Gohda, H. Suzuki, S. Kawahara, and T. Irie, *J. Org. Chem.*, 1964, **29**, 2282.

cyclic fragment ions. The mass spectrum of the nitron B showed a significant difference from that of the nitron A. Beside the molecular ion at m/e 462 (15%), peaks at m/e 309/308 (25.0/100%),* and 112 (20%) were present. The former was assignable to the fragment *F*,



which corresponds to the fragment *D* of the nitron A and the latter was the heterocyclic fragment. In addition to these fragments significant peaks at m/e 306 (27%), 155 (20%), and 113 (10%), which seemed to arise from McLafferty rearrangement as in the case of the 23-ketone (5), were present. The peak at m/e 306 was assignable to the fragment *G* and the rest of the peaks to the fragments *A* and *B*.

It should be noted that whereas the intensity of the aza-steroidal fragment *D* from the nitron A was only 8.9%, that of the corresponding fragment *F* from the nitron B with a 23-oxo-group was 100%.

Cross-over Experiments.—The cross-over experiments were performed by irradiating a mixture of equivalent amounts of either a mixture of AN-14 and BN-15 or a mixture of AN-15 and BN-14 in toluene and in methanol. In each case, a mixture of the nitrites was partially photolysed and the two nitrones and the two starting

* In our preliminary communication² a slightly higher value was reported.

nitrites were separated by preparative t.l.c. For example, when a mixture of AN-14 and BN-15 was partially photolysed in toluene, the nitrones A and B were obtained in 37 and 42% yield, respectively, together with the nitrites A (25%) and B (25%). Photolysis of

the same nitrite mixture was also performed in methanol and in this case the nitrones A and B were obtained in 11 and 7% yields (Scheme 3).

The $^{15}\text{N} : ^{14}\text{N}$ ratios in the nitrones A and B obtained

TABLE 2
 $^{14}\text{N} : ^{15}\text{N}$ Ratios in the nitrones obtained by the cross-over experiments

Nitrite mixture irradiated	Solvent	Nitron obtained	$^{14}\text{N} : ^{15}\text{N}$ ratio
1 AN-14 + BN-15	Toluene	{A	1.22 : 1 ^a
		{B	0.99 : 1 ^b
2 AN-15 + BN-14	Toluene	{A	1.22 : 1
		{B	0.84 : 1
3 AN-14 + BN-15	Methanol	{A	1.28 : 1
		{B	1.06 : 1

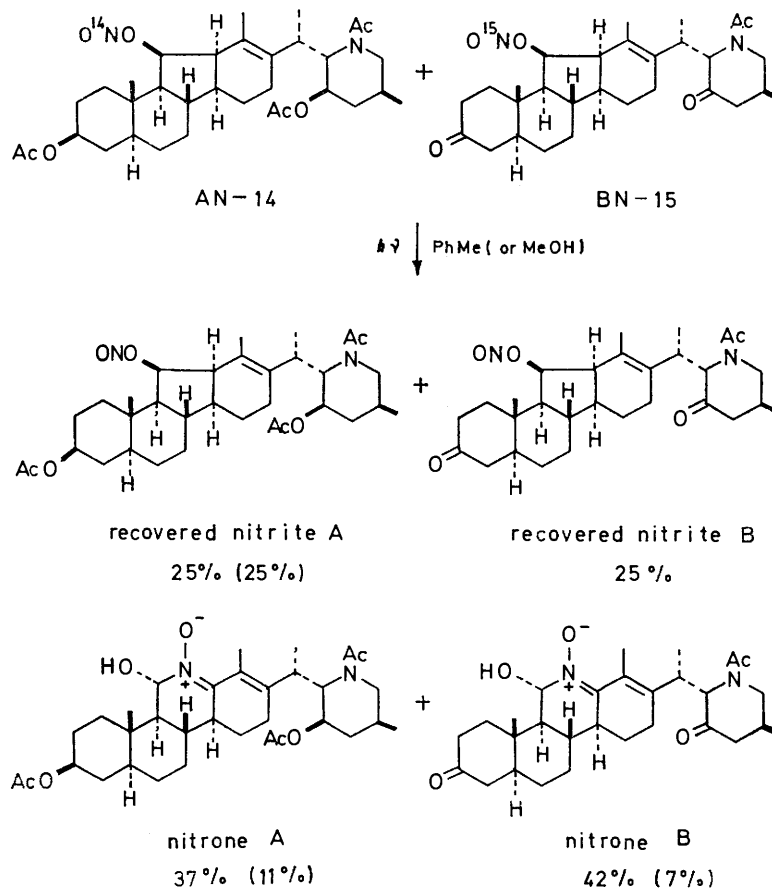
^a An incorrect ratio (2.7 : 1) was given in our preliminary communication.² ^b An incorrect ratio (2.3 : 1) was given in our preliminary communication.²

from the above cross-over experiments were then determined by mass spectrometry, by measurements on the aza-steroidal fragments corresponding to *E* and *F*

of the pure nitrones with ^{14}N . The $^{15}\text{N} : ^{14}\text{N}$ ratios in the nitrones A and B obtained from the three photolyses in either methanol or toluene are shown in Table 2.

The results show that ^{15}N and ^{14}N were randomly

BN-15 was again irradiated in toluene to afford the nitrone A. The $^{14}\text{N} : ^{15}\text{N}$ ratio in this nitrone A was determined by mass spectrometry. The results of three experiments are shown in Table 3.



SCHEME 3

distributed in both nitrones A and B obtained from the photolysis in toluene or methanol.

Each of the two nitrites recovered from the above partial photolysis was then irradiated in either toluene

TABLE 3

$^{14}\text{N} : ^{15}\text{N}$ Ratio in the nitrones obtained from photolysis of the nitrites recovered in the cross-over experiments.

Nitrite irradiated	Solvents	Nitrone obtained	$^{14}\text{N} : ^{15}\text{N}$ ratio
1 Nitrite A from AN-14 + BN-15	Methanol	A	1 : 0.01
2 Nitrite A from AN-14 + BN-15	Toluene	A	1 : 0.01
3 Nitrite B from AN-14 + BN-15	Toluene	B	0.08 : 1

or methanol. In a typical experiment the nitrite A recovered from irradiation of a mixture of AN-14 and

DISCUSSION

The results have several mechanistic implications. First, they prove the intervention of a discrete allyl radical intermediate (C) and disallow synchronous formation⁶ of the nitroso-aldehyde(s) (D^1) and (D^2) from the 11β -nitrite (Scheme 1). Secondly, the results of the photolysis of the recovered nitrites prove that in the initial reversible step in the nitrite photolysis (Scheme 1) the formation of the nitrite from the oxyl radical B and nitrogen monoxide proceeds *via* recombination of the original radical pair. This means that the observed scrambling between ^{15}NO and ^{14}NO in the cross-over experiments took place only in the subsequent stages of the reaction. These results are similar to those⁷ obtained by Akhtar and Pechet for NO migration in the Barton reaction. Since we have shown that the overall quantum yield for nitrone formation in the present reaction is less than unity,⁴ the nitroso-aldehyde (D^1)

⁶ C. S. Coe and T. F. Doumani, *J. Amer. Chem. Soc.*, 1948, **70**, 1516.

⁷ M. Akhtar and M. M. Pechet, *J. Amer. Chem. Soc.*, 1964, **86**, 265.

and/or (D²) must be formed by the combination of nitrogen monoxide and the allyl radical (C).*

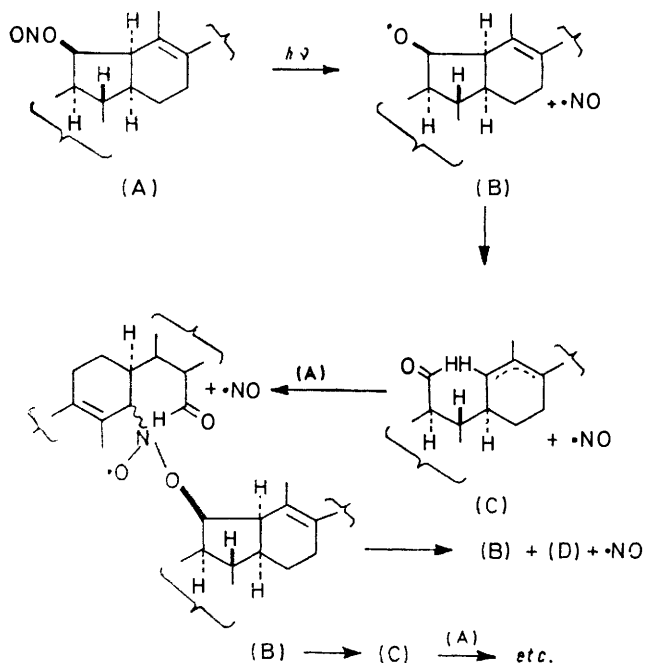
EXPERIMENTAL

For instruments and general procedures see Part 31.¹

Reduction of (22S,25S)-3 β ,23 β -Dihydroxy-5 α -veratr-13(17)-enine-11-one (1).—Lithium aluminium hydride (0.5 g) was added to a solution of the 11-one (1.67 g) in dry tetrahydrofuran (80 ml). The solution was refluxed for 160 min. After careful decomposition of the excess of hydride with ethyl acetate, ethanol, and water, the inorganic material was filtered off. The filtrate was extracted with ether and water. The organic layer was washed with water, dried (Na₂SO₄), and evaporated to leave the crude 11 β -ol (2), which was recrystallized from acetone to yield a *monosolvate* (0.99 g), m.p. 112–114° (Found: C, 73.55; H, 10.6; N, 2.95. C₂₇H₄₅NO₃·Me₂CO requires C, 73.55; H, 10.5; N, 2.85%), ν_{\max} 3 200–3 600br (OH), 1 037 (C–O), and 1 719 cm⁻¹ (acetone), *m/e* 431 (M⁺).

(22S,25S)-N-Acetyl-5 α -veratr-13(17)-enine-3 β ,11 β ,23 β -triol 3,23-Diacetate (3).—The 11 β -ol (2) (823 mg) was partially dissolved in pyridine (15 ml), and to this solution acetic anhydride (7 ml) was added. The solution was stirred at room temperature for 24 h. After the decomposition of the excess of acetic anhydride with methanol, the solvent was removed with added toluene under reduced pressure. The yellow residue was dissolved in chloroform. The solution was washed with 2N-hydrochloric acid and water

* There is an alternative possibility with regard to the mode of scrambling, namely a free radical chain mechanism such as depicted in the following Scheme. Professor J. K. Kochi (personal communication) has pointed out likelihood of this pathway since the concentrations of nitrogen oxide and the species (C) at the steady state in the present reaction are probably very low. However, this mechanism can perhaps be discounted on the following grounds: (a) the quantum yield (although it is an overall yield) of the nitron from the nitrite is less than unity;⁴ (b) the reacting radical centre of the allyl radical (C) is in a crowded environment and attack at the nitrite nitrogen of (A) by the species (C) would probably be prevented by steric interference.



dried (Na₂SO₄), and evaporated and the residue (1.4 g) was recrystallized from ethanol to yield the *triacyetyl derivative* in two crops (730 mg), m.p. 197–198° (Found: C, 71.15; H, 9.2; N, 2.55. C₃₃H₅₁NO₆ requires C, 71.05; H, 9.2; N, 2.5%), ν_{\max} 3 463 (OH), 1 737 (OAc), 1 638 (NAc), and 1 024 cm⁻¹ (C–O); for n.m.r. see Table 1; *m/e* 558 (M + 1) (0.4%), 358 (1.2), 198 (98.6), 156 (100), and 114 (13.9).

(22S,25S)-N-Acetyl-5 α -veratr-13(17)-enine-3 β ,11 β ,23 β -triol (4).—To the triacyetyl derivative (3) (1 g) in methanol (10 ml) was added aqueous methanolic 10% potassium hydroxide. The solution was stirred for 20 h at room temperature, then neutralized with aqueous 2N-hydrochloric acid, and poured into water (200 ml). The crystals were filtered off (926 mg). Recrystallization from ethanol-water gave the *triol*, m.p. 198–200° (Found: C, 72.7; H, 10.0; N, 2.75. C₂₉H₄₇NO₄ requires C, 73.55; H, 10.0; N, 2.95%), ν_{\max} 1 615 (NAc) and 3 320 cm⁻¹ (OH); for n.m.r. see Table 1; *m/e* 114 (33%), 156 (100), *m/e* 316 (0.7), and 473 (M⁺) (0.1).

Oxidation of the Triol (4) with the Savett Reagent.—Chromic anhydride (2 g) was added in portions with stirring to the triol (900 mg) in pyridine (20 ml) at 0 °C. A yellow complex was formed and the solution was stirred for 4 h at room temperature. Saturated aqueous NaHSO₃ was added and the solution was filtered and extracted with chloroform. The extract was washed with aqueous 2N-hydrochloric acid and water, dried (Na₂SO₄), and evaporated. The greenish residue was then passed through a column of alumina. The product (437 mg) was recrystallized from ethanol-water to yield (22S,25S)-N-acetyl-11 β -hydroxy-5 α -veratr-13(17)-enine-3,20-dione (5) (228 mg), m.p. 161–163° (from acetone) (Found: C, 74.3; H, 9.1; N, 2.8. C₂₉H₄₅NO₄ requires C, 74.15; H, 9.25; N, 3.0%), ν_{\max} 1 614 (Nac), 1 714 (six-membered ring ketone), and 3 480 cm⁻¹ (OH); for n.m.r. see Table 1; for *m/e* see text.

Nitrosation of (22S,25S)-N-Acetyl-5 α -veratr-13(17)-enine-3 β ,11 β ,23 β -triol 3,23-Diacetate.—(a) *With nitrosyl chloride and pyridine.* The triacyetyl derivative (3) (2 g) was dissolved in dry pyridine (10 ml), and nitrosyl chloride in pyridine was added dropwise at ca. –20 °C. The solution was poured into water (100 ml) containing ice. The nitrite (7) was filtered off (2.07 g), m.p. 191–193°. After recrystallization from ether it melted at 200–201°.

(b) *With sodium nitrite and acetic acid.* The 11 β -ol (50 mg) in hot acetic acid (1.3 ml) (bath temp. 50–60 °C) was treated with sodium nitrite (25 mg) for 30 s. The mixture was then diluted with water (2 ml) and the resulting crystalline nitrite was filtered off, washed with water, and dried (yield 47 mg); ν_{\max} 1 630 (Nac including N=O str.), 1 736 (OAc), 816, 803, 775 (N–O str.), 1 235, and 1 025 cm⁻¹; for n.m.r. see Table 1.

Photolysis of the Nitrite (7).—The nitrite (656 mg) in toluene (30 ml) in a Pyrex vessel was irradiated with a 100 W high-pressure Hg arc in a nitrogen atmosphere for 7 h. The solvent was removed below 30 °C, and the residue was dissolved in chloroform. The solution was washed with water (twice), dried (Na₂SO₄), and evaporated. Recrystallization of the residue from ether afforded (22S,25S)-N-acetyl-11a-aza-c-homo-5 α -veratra-11a,13(17)-diene-3 β ,11 β ,23 β -triol 11a-oxide (nitron A) (231 mg). Removal of the solvent from the filtrate left a residue (452 mg). Preparative t.l.c. of this (in ethyl acetate) afforded more of the nitron (176 mg), m.p. 144–146° (total yield 62%) (Found: C, 67.3; H, 8.55; N, 4.7. C₃₃H₅₀N₂O₇ requires C, 67.55;

H, 8.6; N, 4.75%), λ_{\max} (EtOH) 285 nm (ϵ 15 800), ν_{\max} 1 547 w (C=N), 1 625 (NAC), 1 732 (OAc), and 3 200—3 600 cm^{-1} (associated OH); for n.m.r. see Table 1; for mass spectral data for the determination of isotope content, see Table 4.

TABLE 4

	<i>m/e</i>	Relative intensity
<i>M</i> — 262 peak	323	0
Isotope peak for <i>M</i> — 262 peak	324	100
	325	21.9

Nitrosation of (22S,25S)-N-Acetyl-11 β -hydroxy-5 α -veratryl-13(17)-enine-3,23-dione with Sodium Nitrite.—The 11 β -ol (32 mg) in hot acetic acid (1 ml) (bath temp. 50—60 °C) was treated with NaNO₂ (20 mg) for 30 s. The mixture was then diluted with water and the resulting crystalline nitrite (9) was filtered off, washed with water, and dried (yield 30 mg).

Photolysis of the Nitrite (9).—The nitrite (9) (250 mg) in toluene (10 ml) was irradiated under argon for 4.5 h as for the nitrite (7). Small amounts of crystals appeared in the solution and were dissolved by addition of methanol. Removal of the solvent left a residue which was dissolved in chloroform. The solution was washed with water, dried (Na₂SO₄), and evaporated. The residue was recrystallized from acetone to yield (22S,25S)-N-acetyl-11 β -hydroxy-11a-aza-c-homo-5 α -veratryl-11a,13(17)-diene-3,20-dione 11a-oxide (nitrone B) (82 mg), m.p. 199—200°, λ_{\max} (EtOH) 288 nm (ϵ 16 500), ν_{\max} 1 630 (NAC), 1 717 (six-membered ring ketone), and 3 300 cm^{-1} (associated OH); for n.m.r. see Table 1 (Found: C, 68.2; H, 7.85; N, 4.6. C₃₃H₄₆N₂O₇ requires C, 68.0; H, 7.95; N, 4.8%), for mass spectral data for the determination of isotope content see Table 5.

TABLE 5

	<i>m/e</i>	Relative intensity
<i>M</i> — 190 peak	307	8.3
Isotope peak for <i>M</i> — 190 peak	308	100
	309	25.0

Nitrosation of (22S,25S)-N-Acetyl-5 α -veratryl-13(17)-enine-3 β ,11 β ,23 β -triol 3,23-Diacetate with Sodium [¹⁵N]Nitrite.—The 11 β -ol (210 mg) in hot acetic acid (2.5 ml) (bath temp. 50—60 °C) was treated with Na¹⁵NO₂ (100 mg) for 30 s (Merck, Sharp & Dohme; ¹⁵N 95.61 atom %). The mixture was then diluted with water (20 ml) and the nitrite (6) filtered off, washed twice with aqueous 5% NaHCO₃ and several times with water, and dried *in vacuo* (yield 198 mg).

Nitrosation of (22S,25S)-N-Acetyl-11 β -hydroxy-5 α -veratryl-13(17)-enine-3,23-dione with Sodium [¹⁵N]Nitrite.—The 11 β -ol (200 mg) in hot acetic acid (2.5 ml) (bath temp. 50—60 °C) was treated with Na¹⁵NO₂ (100 mg) for 30 s (Merck, Sharp & Dohme; ¹⁵N 95.61 atom %). The mixture was diluted with water (2 ml); the precipitate, collected by filtration (193 mg), showed a single spot on t.l.c. After recrystallization from acetone the nitrite (8) showed m.p. 165—166.5°, ν_{\max} 1 641 (NAC), 1 716 (OAc), 1 603 (N=O str.), 723, 750, 760, and 794 cm^{-1} (N—O str.); for n.m.r. see Table 1.

Photolysis of Nitrites.—(a) *Photolysis of the nitrites AN-14 and BN-15 in toluene.* A solution of the nitrites AN-14 (214 mg, 0.365 mmol) and BN-15 (182 mg, 0.365 mmol) in toluene (18.2 ml) was irradiated at room temperature with a 100 W high-pressure Hg arc for 8 h, while argon was bubbled

through slowly. The solvent was removed below 30 °C, and the residue (412 mg) was dissolved in chloroform. The solution was washed with water, dried (Na₂SO₄), and evaporated. T.l.c. of the amorphous residue revealed two major spots and two less polar faint spots due to the two starting nitrites. On addition of acetone to this residue, crystals of the nitrone B (57 mg) were obtained. The residue from the filtrate was submitted to preparative t.l.c. (acetone-benzene, 1:2). Extraction of the most polar component (*R_F* 0) afforded more crude nitrone B, which was recrystallized from acetone (19 mg; m.p. 188—189°) (total yield 42%). Extraction of the second most polar fraction afforded material (103 mg) which was recrystallized from ether to afford the nitrone A, m.p. 144—145° (79 mg, 37%). Mass spectral data are in Table 6.

TABLE 6

	<i>m/e</i>	Relative intensity	
Nitrone A	<i>M</i> — 262(¹⁴ N)	324	53
	<i>M</i> — 262(¹⁵ N) + isotope peak for <i>m/e</i> 324	325	55
	Isotope peak for <i>m/e</i> 325	325	12
Nitrone B	<i>M</i> — 190(¹⁴ N)	308	56
	<i>M</i> — 190(¹⁵ N) + isotope peak for <i>m/e</i> 308	309	66
	Isotope peak for <i>m/e</i> 309	310	15

(b) *Photolysis of the nitrites AN-15 and BN-14 in toluene.* A solution of the nitrites AN-15 (97 mg, 0.165 mmol) and BN-14 (82 mg, 0.165 mmol) in toluene (8 ml) was irradiated at room temperature with a 100 W high-pressure Hg arc for 5 h, while argon was bubbled through slowly. The solid which appeared was dissolved by adding methanol. The solvent was removed and the amorphous residue was subjected to preparative t.l.c. to give the crude nitrones A and B. The nitrone A was recrystallized from ether (yield 27 mg) and the nitrone B from acetone (yield 18 mg). Mass spectral data are in Table 7.

TABLE 7

	<i>m/e</i>	Relative intensity	
Nitrone A	<i>M</i> — 262(¹⁴ N)	324	100
	<i>M</i> — 262(¹⁵ N) + isotope peak for <i>m/e</i> 324	325	104
	Isotope peak for <i>m/e</i> 325	326	23
Nitrone B	<i>M</i> — 190(¹⁴ N)	308	45
	<i>M</i> — 190(¹⁵ N) + isotope peak for <i>m/e</i> 308	309	50
	Isotope peak for <i>m/e</i> 309	310	8

(c) *Photolysis of the nitrites AN-14 and BN-15 in methanol.* A solution of the nitrites AN-14 (130 mg, 0.22 mmol) and BN-15 (110 mg, 0.22 mmol) in dry methanol (11.0 ml) was irradiated at room temperature with a 100 W high-pressure Hg arc for 3 h. The solvent was removed and the residue was dissolved in chloroform. The solution was washed with water (twice), dried (Na₂SO₄), and evaporated. The residue was subjected to preparative t.l.c. (acetone-benzene, 1:2). Four fractions (1—4) were obtained (numbered in order of increasing polarity). Fraction 1 (32 mg) was the crude triacetyl nitrite (nitrone A) and fraction 2 (29 mg) was crude oxo-nitrite (nitrone B). Fraction 3 was crude nitrone A, which was recrystallized from ether (yield 14 mg). Fraction 4 was crude nitrone B, which was recrystallized from acetone (yield 8 mg). Mass spectrometric analysis (Table 8) showed ¹⁴N : ¹⁵N

1.28 : 1 and 1.06 : 1 in nitrones A and B, respectively. The recovered (22*S*,25*S*)-*N*-acetyl-5 α -veratr-13(17)-enine-3 β ,11 β ,23 β -triol 3,23-diacetate 11-nitrite obtained in this experiment was immediately subjected again to photolysis.

TABLE 8

	<i>m/e</i>	Relative intensity	
Nitrone A	<i>M</i> - 262(¹⁴ N)	324	88
	<i>M</i> - 262(¹⁵ N) + isotope peak for <i>m/e</i> 324	325	88
	Isotope peak for <i>m/e</i> 325	326	9
Nitrone B	<i>M</i> - 190(¹⁴ N)	308	49
	<i>M</i> - 190(¹⁵ N) + isotope peak for <i>m/e</i> 308	309	55
	Isotope peak for <i>m/e</i> 309		15

(d) *Photolysis in toluene of the nitrite A recovered from the photolysis of nitrites AN-14 and BN-15 in methanol.* The crude triacetyl nitrite (32 mg), obtained as above, in toluene (2 ml) was irradiated for 5 h. After removal of the solvent the nitrone A was obtained by preparative t.l.c., and was recrystallized from ether (yield 5 mg); for mass spectral data see Table 9.

TABLE 9

	<i>m/e</i>	Relative intensity	
Nitrone A	<i>M</i> - 262 peak	324	83
	<i>M</i> - 262(¹⁵ N) + isotope peak for <i>m/e</i> 324	325	19
	Isotope peak for <i>m/e</i> 325	326	4

(e) *Photolysis in toluene of the nitrites A and B recovered from the photolysis of the nitrites AN-14 and BN-15 in toluene.* A solution of the nitrites AN-14 (130 mg, 0.22 mmol) and

the BN-15 (110 mg, 0.22 mmol) in toluene (11 ml) was irradiated at room temperature with a 100 W high-pressure Hg arc for 3 h under argon. Removal of the solvent under reduced pressure left a residue which was subjected to preparative t.l.c. The least polar fraction (59 mg) was recrystallized from ether to afford 32 mg of crystalline triacetyl nitrite. The second least polar fraction (42 mg) was recrystallized from acetone to yield 27 mg of crystalline oxo-nitrite. The triacetyl nitrite (32 mg) was dissolved in toluene (2 ml) and irradiated under conditions similar to those in the initial photolysis for 3 h 20 min. The solvent was removed and the residue recrystallized from ether to afford the nitrone A (13 mg). The oxo-nitrite (27 mg) was dissolved in toluene (2 ml) and irradiated for 3 h. Removal of the solvent and the recrystallization of the residue from acetone afforded the crystalline nitrone B (6 mg). Mass spectral data are given in Table 10.

TABLE 10

	<i>m/e</i>	Relative intensity	
Nitrone A	<i>M</i> - 262 peak	324	66
	<i>M</i> - 262(¹⁵ N) + isotope peak for <i>m/e</i> 324	325	15
	Isotope peak for <i>m/e</i> 325	326	2
Nitrone B	<i>M</i> - 190(¹⁴ N)	308	11
	<i>M</i> - 190(¹⁵ N) + isotope peak for <i>m/e</i> 308	309	70
	Isotope peak for <i>m/e</i> 309	310	18

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