

Photoinduced Transformations. Part 38.¹ Photoreactions of 17-Ethoxycarbonylmethylene-etiojerva-5,13(17)- and -5,16-diene-3 β ,11 β ,20 ξ -triol 3,20-Diacetate 11-Nitrites

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Photolysis of one of the title nitrites (5) in benzene with a Pyrex-filtered light afforded a complex mixture including as major products 17-ethoxycarbonylmethylene-etiojerva-5,13(17)-diene-3 β ,11 β ,20 ξ -triol 3,20-diacetate (4), 17-ethoxycarbonylmethylene-11a-aza-c-homoetiojerva-5,8,11,12(14),13(17)-pentaene-3 β ,20 ξ -diol 3,20-diacetate 11a-oxide (6), and 17-ethoxycarbonylmethylene-11a-aza-c-homoetiojerva-5,11a,13(17)-triene-3 β ,11 α ,20 ξ -triol 3,20-diacetate 11a-oxide (7); in contrast, photolysis of *N*-acetyl-(22*S*,25*S*)-5 α -veratr-13(17)-enine-3 β ,11 β ,23 β -triol 3,23-diacetate 11-nitrite (1) having a 12 α -hydrogen is known to give (22*S*,25*S*)-*N*-acetyl-11a-aza-c-homo-5 α -veratr-11a,13(17)-diene-3 β ,11 α ,23 β -triol 11a-oxide (2) as the sole product. The formation of the nitron (7) having an α -oriented hydroxy-group supports the mechanism of the rearrangement previously proposed. An estimation by an empirical force-field method with a model hydrocarbon indicates that the five-membered ring of the nitrite (5) is more strained than that of the nitrite (1) by *ca.* 6 kcal mol⁻¹. Thus, the difference in the products obtained from the nitrites (1) and (5) may be attributable to a difference in the polar effects of the C-17-substituents which influence the degree of stabilization of the polar transition state.

The result of the photolysis of 17-ethoxycarbonylmethylene-etiojerva-5,16-diene-3 β ,11 β ,20 ξ -triol 3,20-diacetate 11-nitrite (10) is also described.

WE have previously² reported the formation of an α -hydroxy nitron (2) *via* photoinduced rearrangement of a steroidal cyclopentyl nitrite (1). On the basis of several pieces of experimental evidence,^{2b,c} the rearrangement was shown to proceed *via* the pathway depicted in Scheme 1.

An interesting feature of this photorearrangement was its stereo- and regio-selectivities. Thus, in this photo-rearrangement, a single nitron with an α -oriented 11-hydroxy-group was produced exclusively and no product derived from the nitroso-aldehyde (E) formed by combination between NO and the C-17 end of the allyl radical (B), was obtained. An alternative mode of the nitron formation, which involved an intramolecular migration of 12 α -hydrogen of the nitroso-aldehyde (C) to the formyl carbonyl, was excluded on the basis of the result of the cross-over experiments with unlabelled and ¹⁵N-labelled nitrites.^{2c}

In connection with this pathway, we were interested in a problem of how the configuration of the C(12)-H of

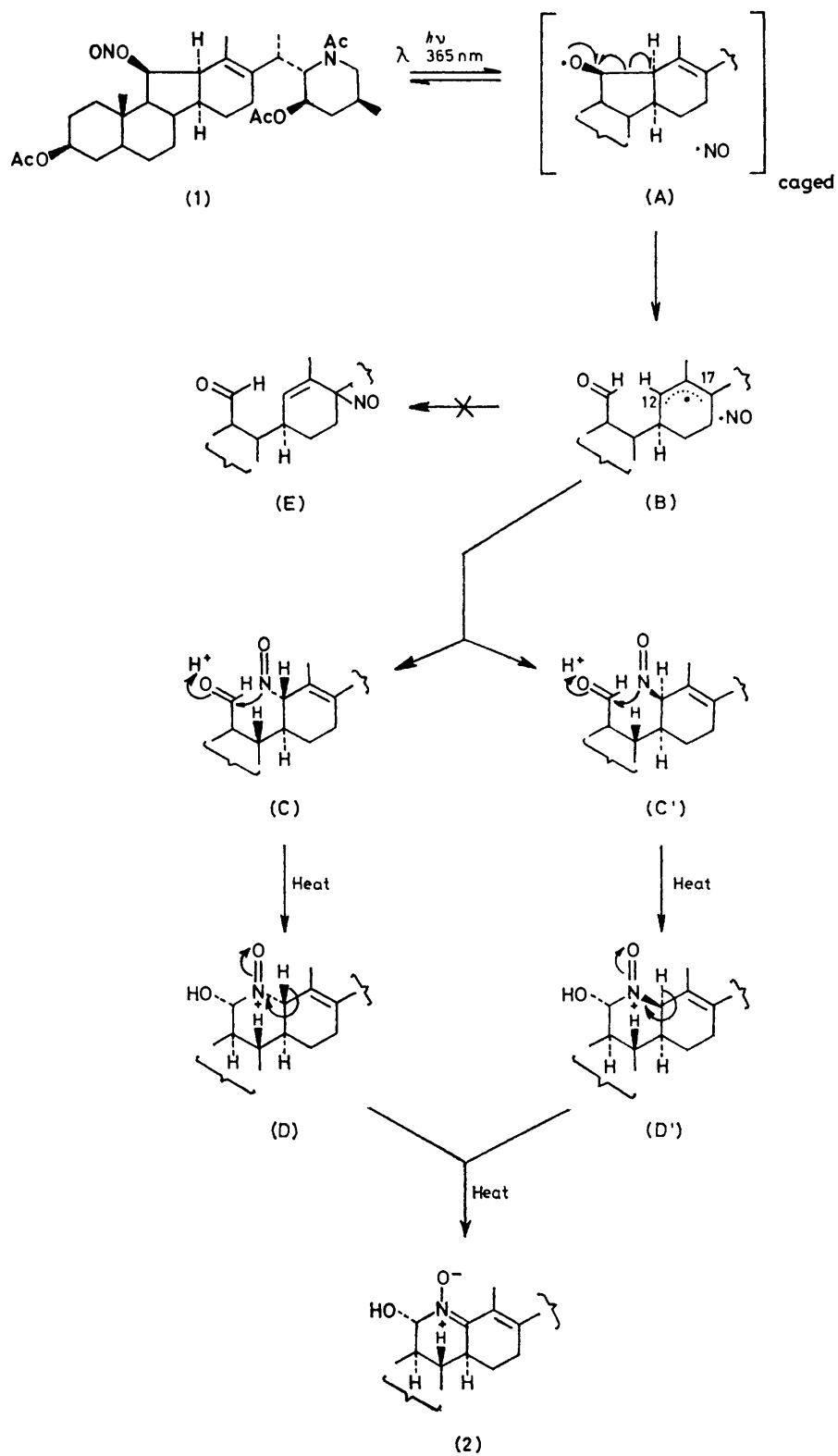
the nitrite (1) influences the products and their stereochemistry in this photoreaction. In the present study, the photolysis of the title nitrite (5), which has *trans*-fused hydrind-6-en-1-ol nitrite part structure (F), is described. The result is compared with that in the photolysis of the nitrite (1) with *cis*-fused hydrind-6-en-1-ol nitrite unit (H) reported previously.² The photolysis of the related nitrite having *trans*-fused hydrind-5-en-1-ol part structure (G) is also described.

RESULTS

Preparations and Photolysis of the Nitrites (5) and (10) (Schemes 2 and 3).—The C-12 epimer of the nitrite (1) is not easily accessible and 17-ethoxycarbonylmethylene-etiojerva-5,13(17)-diene-3 β ,11 β ,20 ξ -triol 3,20-diacetate 11-nitrite (5), which possessed the required structural unit (F), was chosen as the model since the parent triol (3) has

² (a) H. Sugimoto, N. Sato, and T. Masamune, *Tetrahedron Letters*, 1969, 3353; *Tetrahedron*, 1971, **27**, 4863; (b) H. Sugimoto, T. Mizuguchi, and T. Masamune, *J.C.S. Chem. Comm.*, 1972, 376; H. Sugimoto, T. Mizuguchi, S. Honda, and T. Masamune, *J.C.S. Perkin I*, 1977, 927; (c) H. Sugimoto, T. Mizuguchi, and T. Masamune, *Tetrahedron Letters*, 1971, 4723; *J.C.S. Perkin I*, 1976, 2365.

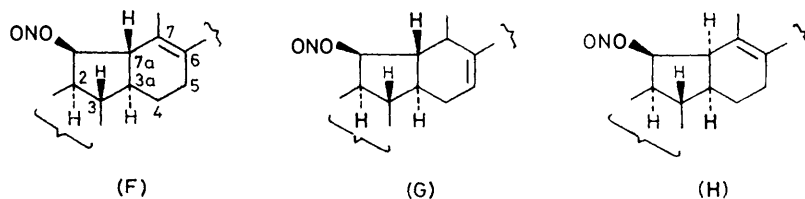
¹ Part 37, H. Sugimoto, N. Yonekura, T. Mizuguchi, and T. Masamune, *Bull. Chem. Soc. Japan*, 1977, **50**, 3010.



SCHEME 1

already been prepared from jervine *via* 10 steps.³ Partial acetylation of the triol (3), obtained by the reported procedure,³ with acetic anhydride and pyridine at room temperature afforded the 3,20-diacetate (4), m.p. 144—146 °C. The electron-impact mass spectrum of the diacetate (4) exhibited no molecular ion. However, two

the diffuse triplet at τ 4.32 to give a sharp singlet. These double-irradiation studies proved that the signals at τ 4.32 and 6.74 are coupled, the latter being assigned to 7 α and 7 β -H and thus supporting our assignment of the signal at τ 4.32. Moreover, the irradiation at τ 7.48 caused changes of the diffuse triplet at τ 4.32 and the singlet at τ 6.74 to a



distinct fragment ions at m/e 414 (41%) and 354 (100%), due to elimination of one and two acetic acid units from the molecular ions, were observed.

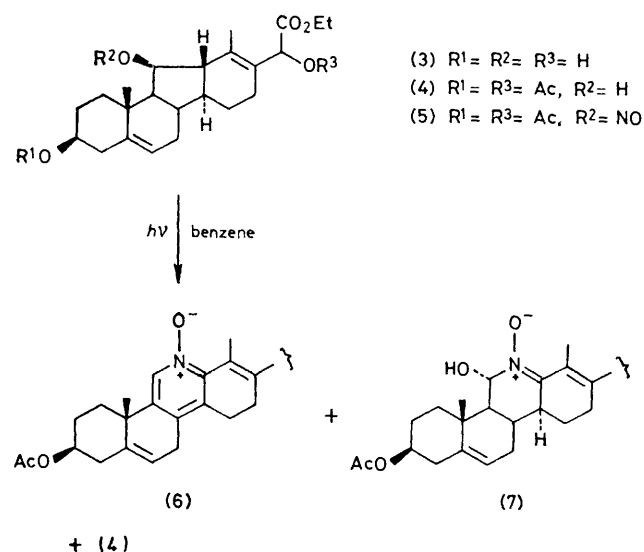
Nitrosation of the diacetate (4) by the usual method afforded an amorphous 11-nitrite (5). The nitrite (5) in benzene was photolysed with a Pyrex-filtered light generated by a 100 W high-pressure Hg arc until photodecomposition was complete. In contrast to the 12 α -nitrite the photoreaction of the 12 β -nitrite (5) was found to result in a complex mixture of several products as revealed by t.l.c. Separation of the products by extensive preparative t.l.c. afforded the parent 11 β -ol (4) (12%), compound (6) (6%), and compound (7) (6%) in the order of decreasing mobilities in t.l.c. together with several minor ill-defined products.

In a mobile fraction, a product having various spectral properties attributable to the corresponding 11-ketone was obtained. However, the structure was not completely confirmed because of lack of material.

The electron-impact mass spectrum of the product (6), m.p. 132—135 °C, exhibited a molecular ion peak at m/e 483. The i.r. spectrum has shown a broad band due to OAc and ester group at 1738 cm^{-1} but no absorption due to the presence of a hydroxy-group. The u.v. spectrum of the product (6) in ethanol exhibited an intense maximum at 206 nm (ϵ 12 700) and two maxima at 265 nm (ϵ 6 590) and 294 nm (ϵ 7 760) with inflection at 304 nm. These absorptions are ascribable to a substituted pyridine *N*-oxide chromophore. This spectral evidence together with the following n.m.r. spectrum supported by double-irradiation studies were in agreement with the pyridine *N*-oxide structure (6): apart from the signals due to 3 α -H, 3-OAc, 20-OAc, 20 ξ -H, 18-H, 19-H, and CO₂Et, the n.m.r. spectrum of the product (6) exhibited three characteristic signals. One of them appeared at τ 1.53 as a sharp 1H singlet. The chemical shift corresponds to α -H of a pyridine *N*-oxide nucleus. Another 1H signal at τ 4.32 is assignable to the C-6 olefinic proton. The shape of this signal differed from that for the 6-H of Δ^5 -steroids and appeared as a diffuse triplet. This suggested a change of conformation of the B-ring in going from the nitrite (1) to the product (6). The third distinct signal appeared as a broad 2H singlet at τ 6.74. By double-irradiation studies it was confirmed that these signals are due to 7 α - and 7 β -H. Thus, irradiation of the 6-H signal caused a change of the broad singlet at τ 6.74 to a singlet ($W_{1/2}$ 4.5 Hz). On the other hand, irradiation of the broad signal at τ 6.74 decoupled

clear triplet ($J = 3.6$ and 3.6 Hz) and a clear doublet ($J = 3.6$ Hz) respectively. This indicated weak allylic coupling between 4-H and 6-H and homoallylic coupling between 4-H and 7-H. Further, it gave the coupling constants of $J_{6,7\alpha}$ and $J_{6,7\beta}$ as 3.6 Hz. The other signals in the n.m.r. spectrum of the product (6) are shown in Table 1.

The mass spectral fragmentation pattern fully supported the assigned structure (6). The spectrum exhibited distinct fragment ion peaks at m/e 467 (66%), 407 (42%), 352 (39%), and 149 (100%). The peak at m/e 467 is due to the loss of



SCHEME 2

oxygen from the molecular ion which is one of the mass spectrometric features of aromatic *N*-oxides.⁴ The peak at m/e 407 is the one which corresponds to the loss of oxygen and acetic acid from the molecular ion.

The u.v., i.r., mass, and n.m.r. spectra of the product (7) were fully in accord with an α -hydroxy-nitrone structure corresponding to the nitron (2). Thus, in the u.v. spectrum of the product (7) in ethanol there were two maxima at 215 (ϵ 6 600) and 294 (ϵ 10 800). In its i.r. spectrum, the product (7) showed a broad band at around 3 400 cm^{-1} due to an associated OH and a band at 1 740

³ T. Masamune, A. Murai, and S. Numata, *Tetrahedron*, 1969, 25, 3145; T. Masamune and T. Orito, *Bull. Chem. Soc. Japan*, 1972, 45, 1888.

⁴ H. Budzikiewicz, C. Djerassi, and D. H. Williams, 'Mass Spectrometry of Organic Compounds,' Holden-Day, Inc., San Francisco, 1967, p. 328.

cm^{-1} due to OAc and CO_2Et . The signal positions and the coupling constants of the n.m.r. spectrum are shown in Table 1. The 11-H signal appeared as a broad doublet at τ 5.10 with $J = 7.5$ Hz. Irradiation at τ 8.1 caused a collapse of this signal to a singlet. This defined the

molecular ion peak but fragment ions at m/e 412 ($M^+ - 2\text{MeCO}_2\text{H}$) (15.3%), 352 (52.4%), and 178 (100%). The last two fragment ions are represented as (a) and (b) (Scheme 4).

Nitrosation of the diacetate (9) afforded an oily nitrite

TABLE I

Chemical shifts (τ) values and coupling constants (Hz) of protons in the etiojervanes and the photoproducts

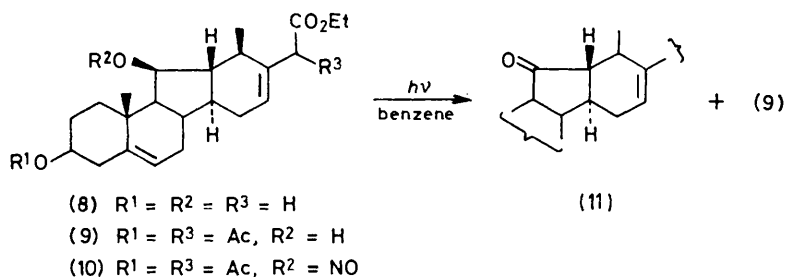
Compd.	3 α -H	6-H	7 α - and 7 β -H	11 α -H or 11 β -H or 11-H	16-H	18-H	19-H	20-H	OAc	OEt
(3)	6.46 (s)	4.72 (bs)	<i>a</i>	5.62 *	<i>a</i>	8.03 (s)	8.70 (s)	4.95 (s)		5.75 (q), 8.71 (t) $J = 7.2$ Hz
(3) ^b	6.50 (bs)	4.72 (bs)	<i>a</i>	5.70 (m)	<i>a</i>	8.07 (s)	8.65 (s)	4.94 (s)		5.75 (q), 8.65 (t) $J = 7$ Hz
(4)	<i>ca.</i> 5.45 (bs)	4.67 (bs)	<i>a</i>	<i>ca.</i> 5.57 †	<i>a</i>	8.02 (s)	8.70 (s)	4.09 (s)	7.84 (s), 7.95 (s)	5.78 (q), 8.74 (t) $J = 7.2$ Hz
(5)	5.41 (bs)	4.65 (bs)	<i>a</i>	3.68 (t) $J = 7.5$ Hz	<i>a</i>	8.27 (s)	8.88 (s)	4.12 (s)	7.85 (s), 7.97 (s)	5.78 (q), 8.68 (t) $J = 7.2$ Hz
(8)	5.33 (bs)	4.32 (bt) ‡	6.74 (bs) ‡	1.53 (s)	<i>a</i>	7.65 (s)	8.51 (s)	3.85 (a)	7.78 (s), 7.90 (s)	5.81 (q), 8.71 (t) $J = 7.2$ Hz
(7)	5.35 (bs)	4.54 (bs)	<i>a</i>	5.10 (bd) ‡	<i>a</i>	7.68 (s)	8.82 (s)	3.99 (s)	7.84 (s), 7.95 (s)	5.76 (q), 8.71 (t) $J = 7.2$ Hz
(7) ^c	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	<i>a</i>	7.33 (s)	8.85 (s)	3.68 (s)	7.82 (s), 7.95 (s)	5.74 (q), 8.82 (t) $J = 7.2$ Hz
(10)	6.49 (bs)	4.72 (bs)	<i>a</i>	*	4.11 (bs)	8.82 (d) $J = 6.9$ Hz	8.71 (s)	5.35 (s)		5.76 (q), 8.74 (t) $J = 7.2$ Hz
(10) ^b	6.50 (bs)	4.75 (bs)	<i>a</i>	5.70 (m)	4.11 (bs)	8.82 (d) $J = 6$ Hz	8.72 (s)	5.36 (s)		5.76 (q), 8.72 (t) $J = 7.2$ Hz
(11)	5.35 (bs)	4.69 (bs)	<i>a</i>	*	4.02 (bs) ($W_{\ddagger} = 12.0$)	8.76 (d) ‡ $J = 6.9$ Hz	8.67 (s)	4.45 (s)	7.81 (s), 7.93 (s)	5.78 (q), 8.71 (t) ‡ $J = 7.2$ Hz
(12)	5.41 (bs)	4.68 (bs)	<i>a</i>	3.83 (bt)	4.01 (bs)	8.99 (d) $J = 6.9$ Hz	8.90 (s)	4.49 (s)	7.82 (s), 7.95 (s)	5.81 (q), 8.71 (t) $J = 7.2$ Hz
(13)	5.32 (bs)	4.53 (bs)	<i>a</i>		3.95 (bd)	8.63 (d) ‡ $J = 6.9$ Hz	8.89 (s)	4.45 (s)	7.81 (s), 7.94 (s)	5.77 (q), ‡ 8.71 (t) ‡ $J = 7.2$ Hz

* Unassignable. ^b Data in literature.³ ^c Data obtained in pyridine.

† Coincided with ethoxy protons. ‡ Confirmed by decoupling; see text on details of decoupling studies on compds. (8) and (9).

chemical shift of 9 α -H of the nitron (7) as *ca.* τ 8.1. The signal due to 19-H was found to shift 0.03 p.p.m. upfield in pyridine relative to deuteriochloroform. This behaviour parallels that of the nitrones obtained previously.^{2a,b} On this basis, an α -configuration is assigned to the 11-OH group of the nitron (7). In the mass spectrum of the

(10) which was photolysed by a procedure comparable to that used for the nitrite (5). In this case, two major and several minor products were also produced. By preparative t.l.c., two major products, 3 β ,20 ξ -dihydroxy-17-ethoxycarbonylmethylene-etiojerva-5,16-dien-11-one (11) and the parent 11 β -ol (9) were obtained in 13



SCHEME 3

nitron (7), the molecular ion was absent but prominent fragment ions at m/e 485 ($M^+ - \text{H}_2\text{O}$), 467 ($M^+ - 2\text{H}_2\text{O}$) (16%), 407 ($M^+ - 2\text{H}_2\text{O} - \text{CH}_3\text{CO}_2\text{H}$) (97%), and 352 (100%) were observed.

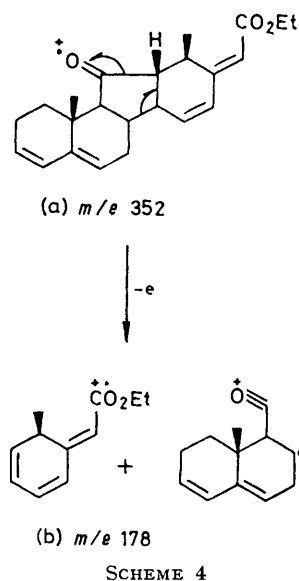
Partial acetylation of 17-ethoxycarbonylmethylene-etiojerva-5,16-diene-3 β ,11 β ,20 ξ -triol (8) afforded the corresponding 3,20-diacetate (9) (Scheme 3).

The mass spectrum of the diacetate (9) has shown no

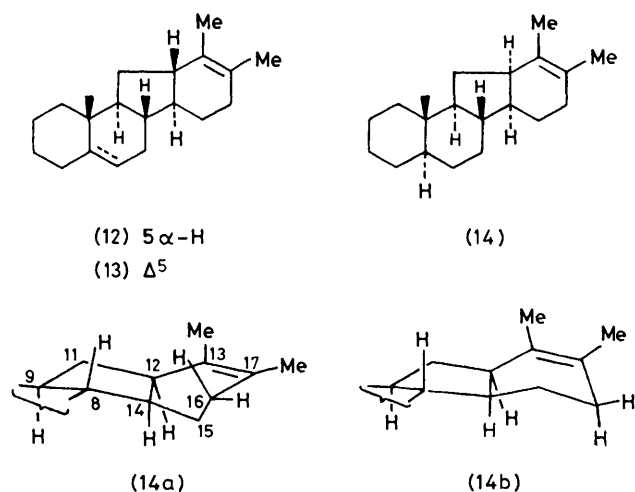
and 17% yields. The former was confirmed by a direct comparison with a specimen obtained by Jones oxidation of the 11 β -ol (9).

An Estimation of the Difference of Steric Energy for the Five-membered Ring of the Nitrites (1) and (5) by a Force-field Method.—One of the most important factors which influences the ease of β -scission of the 11-oxyl radicals would be strain in the five-membered ring. An estimation

has been made of the difference between the degrees of strain for the five-membered c-rings of 17-ethoxycarbonylmethylene-etiojerva-5,16-diene-3 β ,11 β ,20 ξ -triol 3,20-diacetate 11-nitrite (5) and (22*S*,25*S*)-*N*-acetylveratr-13(17)-en-11 β -yl nitrite (1) by a force-field method. In order to calculate the difference, three models having structures



(12), (13), and (24) were used. Examination of Dreiding models corresponding to the structures (12), (13), and (14) indicated that the c,d-rings of the *c/d trans*-structures (12) and (13) were rather rigid while in a model corresponding to structure (14) two major conformers (14a) and (14b) with



regard to the c,d rings were possible. Thus, the conformer (14a) can undergo conformational conversion into an alternative conformer (14b) by inversion at C-16. In the

* The possibility that the observed 11 β -ol was formed *via* a β -scission-recombination process is ruled out since it would lead to a more stable 11 α -ol.⁷

⁵ (a) N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, *J. Amer. Chem. Soc.*, 1971, **93**, 1637; (b) N. L. Allinger and J. T. Sprague, *ibid.*, 1972, **94**, 5734.

conformer (14a) the distance between 8 β -H and 16 β -H is much closer than that in the conformer (14b). Allinger's force field⁵ was used in conjunction with pattern-research

TABLE 2

Calculated energies of model hydrocarbons *

	Heat of formation (kcal mol ⁻¹)	Strain energy (kcal mol ⁻¹)	Sum of steric energy components of C-8, -9, -11, -12 and -14 (kcal mol ⁻¹)
(12)	-45.96	23.04	18.64
(13)	-19.50	24.32	20.83
(14a)	-48.72	20.28	14.97
(14b)	-48.50	20.50	15.32

* Calculations were performed at the Hokkaido University Computing Centre.

energy-minimization technique⁶ to calculate the energies relevant to the present discussion; these are shown in Table 2.

DISCUSSION

The foregoing experiments proved that the nitrones with an α -oriented hydroxy-group at the α -position of the *N*-oxide group are formed in the photo-reaction of *c*-nor-*D*-homo-steroid 11 β -ol nitrites with a 13(17) double-bond, irrespective of the 12-H configuration. This result is consistent with our proposed path for the nitron formation depicted in Scheme 1. Namely, the cyclization of the nitroso-aldehyde [(C) and/or (C')] may lead to the formation of the intermediate D or D' with the α -oriented hydroxy-group since the presence of the 10 β -methyl may prevent the formation of a less stable intermediate with a β -oriented hydroxy-group.^{2b}

The present study has shown that, whereas photolysis of the 11 β -ol nitrite (1) resulted solely in β -scission of the oxyl radical to give the nitron as the sole product, the 11 β -ol nitrite (5) afforded several products including, as major components, the parent 11 β -ol, compound (8) with a pyridine *N*-oxide nucleus, and the nitron (9). This contrast in the photo-products is of interest since the formation of a significant amount of the 11 β -ol indicates that β -scission of 11 β -oxyl radical generated from the nitrite (5) is more difficult than for the oxyl radical generated from the nitrite (1).*

Many factors^{8,9} may influence the relative ease of β -scission¹⁰ of the 11 β -oxyl radicals generated from the *c/d cis*- (1) and *trans*-nitrite (2). However, the most important ones would be the stabilities of both the allyl radical and the product ketone generated, or of the transition state leading to them, and the degree of five-membered ring strain. With regard to the former

⁶ (a) E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1973, **95**, 8005; (b) J. D. Andose, and K. Mislow, *ibid.*, 1974, **96**, 2168.

⁷ N. Sato and T. Masamune, *Tetrahedron Letters*, 1967, 1557; *Bull. Chem. Soc. Japan*, 1969, **42**, 215.

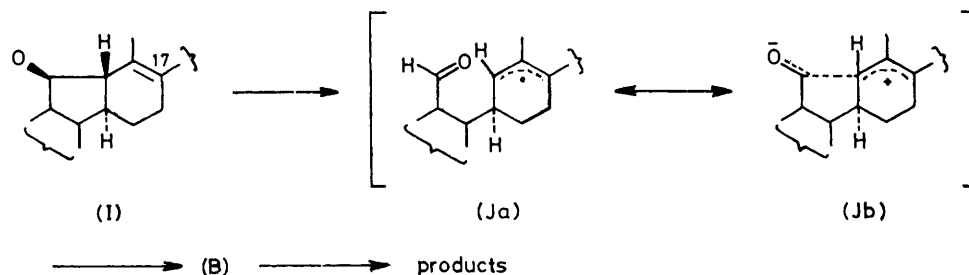
⁸ C. Walling and A. Padwa, *J. Amer. Chem. Soc.*, 1963, **85**, 1593.

⁹ F. D. Greene, M. L. Savitz, F. D. Osterholtz, H. H. Lau, W. N. Smith, and P. M. Zanet, *J. Org. Chem.*, 1963, **28**, 55.

¹⁰ P. Gray and A. Williams, *Chem. Rev.*, 1959, **59**, 239.

factor, the importance of polar effects in the transition state of β -scission has been noticed by Walling¹¹ and Kochi¹² and their colleagues.

Of these factors, an estimation of the difference of the steric energy of the five-membered ring of etiojerva-5,13(17)-diene and 12 α -etiojerva-5,13(17)-diene with the model systems by a force-field method indicated that the sum of steric energy components of the five-membered ring carbons of the *c/D trans*-isomer is some 6 kcal mol⁻¹ larger than that of the *c/D cis*-isomer. Thus, we should expect that provided that ring strain is the most important factor for cleavage, since the nitrite (5) has a more strained five-membered ring, the 11,12-bond may cleave more easily than that of the nitrite (1). In fact, the reverse is found in the present experiments.



In view of the complexity of the molecules, with which we are dealing, the observed difference of the reactivities of two nitrites (1) and (5) cannot be attributed to any single factor. However, having excluded the factor of five-membered ring strain, the observed preference for opening of the five-membered ring of the nitrite (1) over that of the nitrite (5) might be chiefly ascribable to a difference in the degree of the stabilization of the allyl radical intermediate (B) or of the transition state (J) leading to them. Thus, the difference in the products between the nitrites (1) and (5) may, perhaps, be rationalized in terms of the difference of the polar effects^{11,12} of the C-17 substituents which influence the degree of stabilization of the polar transition state (Jb).

The path which leads to formation of the product (6) is not easily explained, there being, at present, no evidence on which to base a mechanism. The product (6) is, however, most probably formed *via* dehydration and oxidation of the nitron (7) during the photoreaction and not simply during the work-up stage since the latter was stable at room temperature. The formation of a heteroaromatic *N*-oxide analogous to the product (6) was not observed in the photoreaction of the nitrite (1). Although it is not clear why the pyridine *N*-oxide is formed, especially in the photolysis of the nitrite (5), it is possible that the nitron ring in the nitrite(s) is destabilized by the 17-substituent.

The results of the photolysis of the nitrite (10) indicate that the strain in the five-membered ring of hydrind-5-

en-1-ol nitrite system is not sufficient to cause β -scission of the oxyl radical generated.

EXPERIMENTAL

For instruments used and general procedures see Part 30.¹³ Preparation of 17-Ethoxycarbonylmethylene-etiojerva-5,13(17)-diene-3 β ,11 β ,20 ξ -triol (3) and 17-Ethoxycarbonylmethylene-etiojerva-5,16-diene-3 β ,11 β ,20 ξ -triol (8).—These compounds were prepared by a described 10-step procedure³ from jervine.

Preparation of 17-Ethoxycarbonylmethylene-etiojerva-5,13(17)-diene-3 β ,11 β ,20 ξ -triol 3,20-Diacetate (4).—The triol (280 mg) in pyridine (5 ml) in the presence of acetic anhydride (0.75 ml) was stirred for 13 h at room temperature. The reaction mixture was worked up as usual to afford the

amorphous diacetate. This was recrystallized from ether-n-hexane to afford crystals of the diacetate (295 mg), m.p. 144–146 °C (Found: C, 68.15; H, 8.1. C₂₇H₃₈O₇ requires C, 68.35; H, 8.05%), ν_{\max} 3507 (OH) and 1721 and 1744 cm⁻¹ (OAc, CO₂Et); $[\alpha]_D^{20}$ -141.7° [*c* 0.83, (MeOH)]; n.m.r. data are given in Table 1.

17-Ethoxycarbonylmethylene-etiojerva-5,13(17)-diene-3 β ,11 β ,20 ξ -triol 3,20-Diacetate Nitrite (5).—The diacetate (196 mg) was dissolved in pyridine (3 ml) and nitrosyl chloride in pyridine was added dropwise at *ca.* -20 °C. The progress of the reaction was monitored by t.l.c. The solution was poured into water and the nitrite was extracted with methylenedichloride. The methylene dichloride solution was washed with water three times and dried (Na₂SO₄). The solvent was removed by rotary evaporator at room temperature to yield an amorphous nitrite (226 mg) which was immediately subjected to photolysis, ν_{\max} (CHCl₃) 1735br (OAc, CO₂Et), 1644, and 824 cm⁻¹ (ONO); n.m.r. data are given in Table 1.

Photolysis of the Nitrite (5).—The nitrite (352 mg) dissolved in dry benzene (15.5 ml) was subjected to photolysis with 100 W high-pressure Hg arc lamp, through Pyrex, under nitrogen. The progress of the reaction was monitored by t.l.c. (Spots due to the nitrite were detected by diphenylamine-sulphuric acid.) All the nitrite decomposed after 9.5 h and the solvent was removed by a rotary evaporator at room temperature to afford a complex mixture of brown oily products (372 mg). This was subjected to preparative t.l.c. (solvent, benzene-ether 5:1). Seven fractions A–G were obtained in the order of decreasing mobilities on t.l.c. The most mobile fractions A (18 mg) and B (14 mg) were not identified. The fraction C (43 mg)

¹¹ C. Walling and P. J. Wagner, *J. Amer. Chem. Soc.*, 1964, **86**, 3368.

¹² J. D. Bacha and J. K. Kochi, *J. Org. Chem.*, 1965, **30**, 3272.

¹³ H. Sugimoto, T. Tsuneno, N. Sato, N. Maeda, T. Masamune, H. Shimanouchi, Y. Tsuchida, and Y. Sasada, *J.C.S. Perkin I*, 1976, 1297.

was purified again by t.l.c. to afford two fractions (C_1 and C_2). The more mobile fraction C_1 (8 mg) was not identified. The i.r. and n.m.r. spectra suggested that the amorphous compound C_2 (6) (11 mg) was probably the corresponding 11-ketone but this was not confirmed. Fraction D (67 mg) was a mixture of several minor compounds and none of the compounds was identified. Fraction E (157 mg) was a mixture of the *N*-oxide (6), the 11 β -ol (4), and the nitrone (7). The mixture was subjected to preparative t.l.c. twice, and three compounds, (6) (21 mg), (4) (41 mg), and (6) (20 mg) were obtained in order of decreasing mobilities. The *N*-oxide (6) was recrystallized from ether to yield an analytical specimen, m.p. 132–135 °C (Found: C, 66.6; H, 7.0; N, 2.8. $C_{27}H_{35}NO_7$ requires C, 66.8; H, 7.3; N, 2.9%). The 11 β -ol was recrystallized from ether. The nitrone (7) was recrystallized from ether to yield an analytical specimen, m.p. 128–132 °C (Found: C, 63.8; H, 7.6; N, 2.6. $C_{27}H_{39}NO_8$ requires C, 64.1; H, 7.8; N, 2.8%). Fraction F (29 mg) and fraction G (75 mg) were complex mixtures and were not identified.

Preparation of 3 β ,20 ξ -Dihydroxy-17-ethoxycarbonylmethylene-etiojerva-5,16-dien-11-one, 3,20-Diacetate (11).—Jones reagent was added dropwise to the 3,20-diacetate (9) (51 mg) in acetone (3 ml). Excess of chromic acid was decomposed with 5% sodium hydrogensulphite and the solution was extracted with ether. The ethereal solution was twice washed with water and dried (Na_2SO_4). After removal of the solvent, the residue (49 mg) was purified by preparative t.l.c. and recrystallized from *n*-hexane–ether to afford the ketone (11) (11 mg), m.p. 167–169 °C (Found: C, 68.45; H, 7.75. $C_{27}H_{36}O_7$ requires C, 68.6; H, 7.7%), ν_{max} 1740 cm^{-1} (CO_2Et , five-membered ring ketone and OAc); n.m.r. data are given in Table 1.

Preparation of 17-Ethoxycarbonylmethylene-etiojerva-5,16-diene-3 β ,11 β ,20 ξ -triol 3,20-Diacetate (9).—The triol (349 mg) in pyridine (8 ml) in the presence of acetic anhydride

(1.0 ml) was stirred for 12 h at room temperature. The reaction mixture was worked up to afford a crude diacetate. This was recrystallized from ethyl acetate–*n*-hexane to afford the diacetate (117 mg) as the first crop, m.p. 141–143 °C (Found: C, 68.35; H, 8.1. $C_{27}H_{38}O_7$ requires C, 68.35; H, 8.05%), ν_{max} 1735 (CO_2Et and OAc) and 3527 cm^{-1} (OH); $[\alpha]_D^{20}$ –140.2° (*c*, 0.90, methanol); n.m.r. data are given in Table 1.

17-Ethoxycarbonylmethylene-etiojerva-5,16-diene-3 β ,11 β ,20 ξ -triol 3,20-Diacetate Nitrite (10).—The diacetate (265 mg) in pyridine (5 ml) was nitrosated as for the isomeric 3,20-diacetate. An oily nitrite (283 mg) obtained was immediately subjected to photolysis; n.m.r. data are given in Table 1.

Photolysis of the Nitrite (10).—The nitrite (283 mg) in dry benzene (13.0 ml) was subjected to photolysis under the same conditions as those for the isomeric nitrite (5). All the nitrite decomposed after 7.5 h. Removal of the solvent left a residue. T.l.c. of the product indicated that it was a mixture of several products including two major products. This was subjected to preparative t.l.c. (solvent, benzene–ether 3 : 1). Six fractions A–F were obtained in order of decreasing mobilities. The most mobile fraction A (34 mg), once purified by preparative t.l.c., was recrystallized from ether–*n*-hexane to yield the 11-ketone (6 mg), m.p. 160–163 °C.

Fraction B (44 mg) was again purified by preparative t.l.c. and recrystallized from *n*-hexane–ether to yield the 11 β -ol (2 mg). Fractions C (24 mg), D (32 mg), E (18 mg), and F (65 mg) were a complex mixture of unidentified compounds.

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