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Some Observations on Photolysis of Fused Cyclopentyl Nitrites[1)]

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The results of photolysis of three fused cyclopentyl nitrites, Ib, VIIIb, XIV, all of which have 22,27-imino-17,23-oxidojervane framework, are described. In all three cases, competition among the reactions of 11-alkoxyl radical, which led to a variety of products, has been observed. However, the cleavage of α,β carbon-carbon bond to the nitrosoxyl group in these compounds is not the major course of the reaction. It has been found that whenever sterically possible (*e. g.*, Ib), 11-alkoxyl radical in these nitrites is capable of achieving the Barton reaction and the reaction leads to relatively few products. In two cases of these photolyses, the reaction is accompanied by epimerization of the relevant alkoxyl radicals. Some aspects of these transformations are considered in the light of other available data.

In connection with other investigations we were interested in the photolysis of 11-ol nitrites in C-nor-D-homosteroid framework which can be derived from readily-available veratrum alkaloid jervine.

In this paper, we shall describe the results of photolysis of three nitrites, all of which have 22,27-imino-17,23-oxidojervane framework, and will discuss some aspects of the observed transformations which are summarized in annexed charts.

We first examined photolysis of 3-*O*,*N*-diacetyl-22,27-imino-17,23-oxidojerv-5-ene-3β,11β-diol 11-nitrite (Ib). The reaction of 11β-ol (Ia)[2)] with nitrosyl chloride in pyridine[3)] readily afforded the corresponding stable nitrite (Ib), mp 208—210°C. This was photolyzed in toluene by a 150 W high pressure mercury arc lamp for 3 hr. The three major compounds produced (see Experimental) were isolated by preparative thin layer chromatography[*1] to afford a new compound (III), mp 234.5—235°C, (5%), 3-*O*,*N*-diacetyl-22,27-imino-17,23-oxidojerv-5-ene-3β,11α-diol (VI)[2)] (27%), and 3-*O*,*N*-diacetyl-22,27-imino-17,23-oxidojerv-5-en-3β-ol-11-one (VII)[4)] (24%). The new compound had a molecular formula $C_{31}H_{46}O_6N_2$ and could immediately be formulated as a 19-oximino derivative (III) of 3-*O*,*N*-diacetyl-22,27-imino-17,23-oxidojerv-5-ene-3β,11β-diol by the NMR spectrum which retained all signals between τ 9.13 and τ 7.5 except that of C-19 methyl protons in the 11β-ol (Ia) and showed a singlet absorption at τ 2.3 due to a methine proton at C-19.[5)]

The second nitrite photolyzed was *N*-acetyl-22,27-imino-17,23-oxidojerv-4-en-11β-ol-3-one 11-nitrite (VIIIb), in which A and B rings of Ib were modified. This nitrite was easily obtainable by partial acetylation of the 11β-alcohol (VIIIa)[2)] followed by nitrosation in usual way. Photolysis was carried out under comparable conditions with the photolysis of Ib. Contrary to the photolysis of Ib, the composition of the reaction product was complex (at least 8 spots on thin layer) and three major products, 11-ketone (IX), 11β-ol (X) and 11α-ol (XI) were isolated after extensive preparative thin layer chromatography in the yield of 3%, 23% and 2%,

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[1)] a) Photoinduced Transformations. V. Part of this work has been reported. H. Suginome, N. Sato and T. Masamune, *Tetrahedron Letters,* **1967**, 1557. Part IV. H. Suginome, M. Murakami and T. Masamune, This Bulletin, **41**, 468 (1968). b) Regarding stereochemistry of jervine, see. J. W. Scott, L. J. Durham, H. A. P. deJongh, U. Burckhardt and W. S. Johnson, *Tetrahedron Letters,* **1967**, 2381. G. N. Reeke, Jr., R. L. Vincent and W. N. Lipscomb, *J. Am. Chem. Soc.*, **90**, 1663 (1968). S. M. Kupchan and M. I. Suffness, *ibid.*, **90**, 2730 (1968). c) The configurations at C-12 and C-13 of dihydrojervine (12αH, 13αH) and hence those of 11β-ol (Ia) were proposed by Wintersteiner and Moore (*Tetrahedron,* **20**, 1947 (1964)). However, our recent work shows that C-12 hydrogen of dihydrojervine is preferably β-configuration (T. Masamune, A. Murai, H. Ono, K. Orito and H. Suginome, *Tetrahedron Letters,* in press). Therefore, in this paper, a series of compounds derived from dihydrojervine will be formulated on the basis of this new evidence.

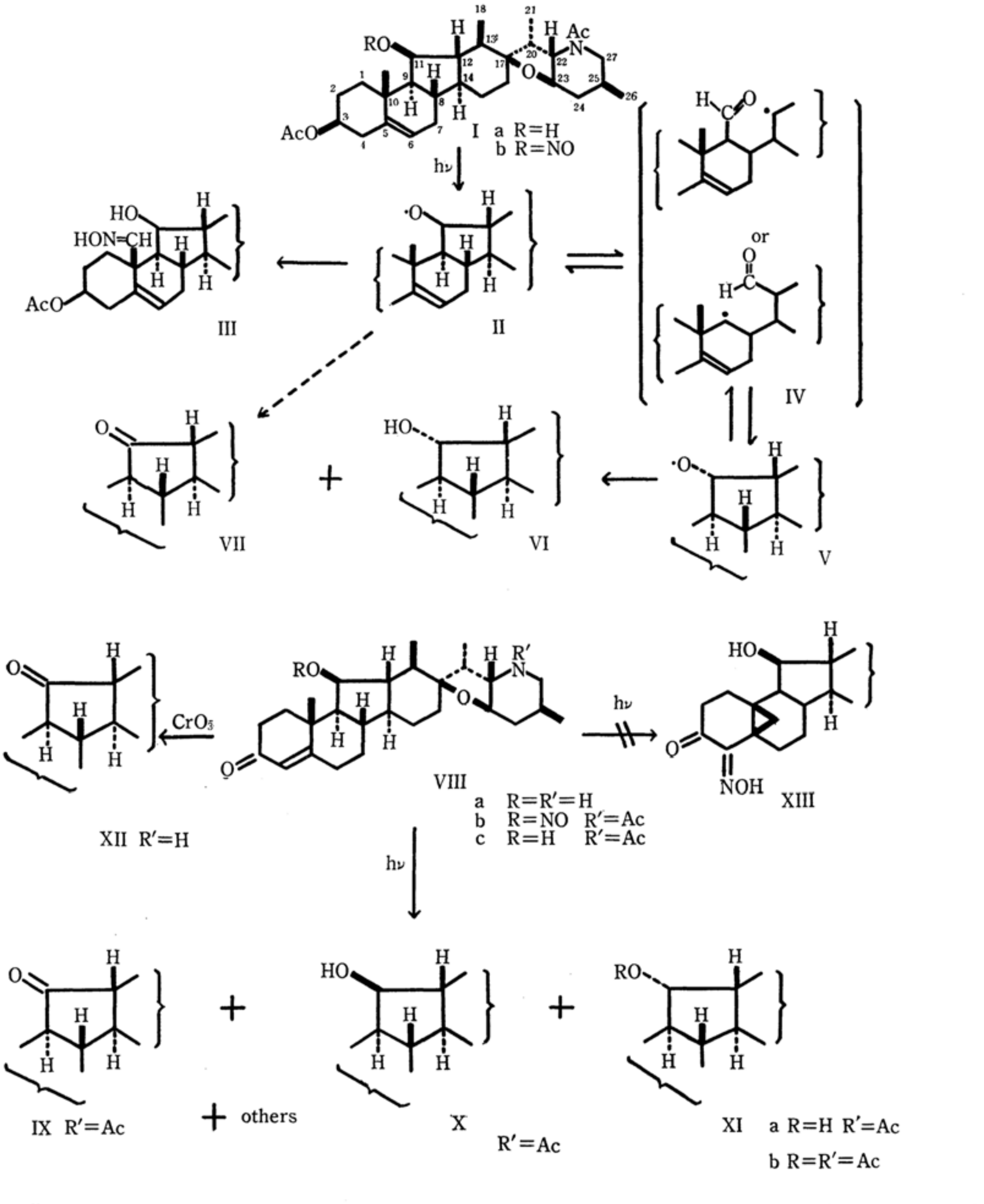
[2)] T. Masamune, N. Sato, K. Kobayashi, Y. Yamazaki and Y. Mori, *Tetrahedron,* **23**, 1591 (1967).

[*1] Yields of the pure compounds from this photolysis are not the same as those described in the preliminary communication.[1)]

[3)] R. H. Pickard and H. Hunter, *J. Chem. Soc.,* **1923**, 434.

[4)] W. A. Jacobs and C. F. Heubner, *J. Biol. Chem.,* **170**, 635 (1947).

[5)] W. D. Phillips, *Ann. N. Y. Acad. Sci.,* **70**, 817 (1958).



respectively.[6] The compounds IX and XI were new compounds and after the spectroscopic identification these were identified by direct comparison with those newly prepared. Thus, VIIIa[2] was oxidized with chromic anhydride-sulfuric acid in DMF to yield the corresponding 11-ketone (XII). The ketone was then acetylated to yield the corresponding *N*-acetyl derivative (IX) which was identical with the ketone obtained from photolysis. The 11α-ol (XIa), on the other hand, was prepared by brief hydrolysis of the corresponding diacetyl derivative (XIb).[2]

Various pathways[7–11] have been found in

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6) All other products were minor and ill-defined, but the absence of 19-oximino compound or substances having cyclopropane ring, was proved by the NMR spectra of the crude product.

7) For reviews, see a) A. L. Nussbaum and C. H. Robinson, *Tetrahedron*, **17**, 35 (1962). b) M. Akhtar in "Advances in Photochemistry," Vol. II, ed. by W. A. Noyes, G. S. Hammond and J. N. Pitts, Jr., Interscience Publishers, New York, N. Y. (1964), p. 263.

8) C. H. Robinson, O. Gnoj, A. Mitchell, R. Wayne, E. Townley, P. Kabasakalian, E. P. Oliveto and D. H. R. Barton, *J. Am. Chem. Soc.*, **83**, 1771 (1961).

photolysis of nitrites of cyclopentanol derivatives, and the competitive nature of β-scission and inter- or intramolecular hydrogen abstraction in simple alkoxyl radical reactions has been extensively investigated.[12]

It is interesting to note that in the two experiments above mentioned and the photolysis of the 11α-ol nitrite XIV (*vide infra*) none of the products which arise from the scission of α,β-carbon-carbon bond of alkoxyl radicals on five-membered ring[8,11] were found in noticeable amounts, and instead, products of the competition among epimerization, hydrogen abstraction and presumed scission of α,β-carbon-hydrogen bond of alkoxyl radicals were observed.

The formation of 11α-ols, VI, XIa, in these reactions would seem to necessitate inquiry into the possible mode of the transformation.

The most likely mechanism for this epimerization would be one involving reversible aldehyde formation such as IV and this pathway has recently been suggested by Wettstein and co-workers[13] and by Akhtar[7b] to interpret an epimerization[9] from α-caryophyllene alcohol nitrite to epi-α-alcohol, which is the only precedent for this type of transformation.[14]

On the other hand, if we assume that reacting cyclopentyl radicals are planer[15] or that they rapidly invert, other pathways such as *via* a rearrangement of the secondary alkoxyl radical, $RR'CH\text{-}O\cdot\rightarrow RR'\dot{C}\text{-}OH\rightarrow RR'CHOH$, or regeneration of the secondary alcohol followed by the loss of α-hydrogen,[16] $RR'CH'\text{-}O\cdot\rightarrow RR'CHOH\rightarrow RR'\text{-}\dot{C}\text{-}OH\rightarrow RR'CHOH$, should also be considered, since these pathways can lead to the formation of both 11α and 11β-ols. In fact, two examples[9] of epimerization, including one of the present experiments, resulted in the isolation of both epimers although the ratio of isolated α- and β-epimers was quite different in each case.[17]

However, in regard to these alternatives, we may point out that if the latter mechanisms operate, alkoxyl radicals in six-membered rings must likewise suffer epimerization. Although a considerable number of results have been accumulated on the photolysis of nitrite esters in the field of normal steroids, epimerization of alkoxyl radical in six-membered ring has never been observed[7] and the epimerizations so far found have all been concerned with nitrite on five-membered rings in which a number of scission reactions has been observed.[8,9,11]

This seems to be in favor of the epimerization *via* reversible process as shown in the chart.

It has been found that no 18-oximino derivatives of 22,27-imino-17,23-oxidojervanes were formed in these photolyses. Exclusive attack by the O-radical on the C-19 methyl suggests that the C-18 methyl is not located in the range of attack of the 11-alkoxyl radical. Inspection of the Dreiding model of the 11β-ol (Ia)[1c] indicates that a plausible conformation of the D ring of this molecule, would be a chair form in which the C-18 methyl would occupy an equatorial position. This conformation leads the C-19 methyl to a nearer position than the C-18 methyl with respect to the 11β-alkoxyl radical,

In the NMR spectra of steroid, additivity of group effects for C-18 and C-19 proton signals was well established[18] and this principle has recently been shown to hold for those protons in jervine derivative.[2] It was expected that the present exclusive attack of the 11β-alkoxyl radical on the C-19 methyl might be correlated to these group effects. In 22,27-imino-17,23-oxidojervane derivatives, the deshielding effect of the 11β-hydroxyl for the C-18 proton signals is only 0.11 ppm and has virtually the same value as that of the 11α-hydroxyl group. However, the deshielding effect of the 11β-hydroxyl group for the C-19 methyl has been found to be 0.295 ppm which is close to the corresponding effects of the 11β-

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9) A. Nickon, J. R. Mahajan and F. J. McGuire, *J. Org. Chem.*, **26**, 3617 (1961).

10) P. Kabasakalian and E. R. Townley, *ibid.*, **27**, 2918 (1962).

11) P. Kabasakalian and E. R. Townley, *ibid.*, **27**, 3562 (1962); M. Nakazaki and K. Naemura, This Bulletin, **37**, 532 (1964).

12) P. Gray and A. Williams, *Chem. Revs.*, **59**, 239 (1959); J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 1193 (1962); C. Walling and A. Padwa, *ibid.*, **85**, 1593 (1963).

13) C. Meystre, K. Heusler, J. Kalvoda, P. Wieland, G. Anner and A. Wettstein, *Helv. Chim. Acta*, **45**, 1317 (1962), footnote 38.

14) Similar epimerization of 11β-hydroxyl group of normal steroid by oxidation with lead tetraacetate has been reported. K. Heusler, J. Kalvoda, G. Anner and A. Wettstein, *Helv. Chim. Acta*, **46**, 352 (1963); G. B. Spero, J. L. Thompson, W. P. Schneider and F. Kagan, *J. Org. Chem.*, **28**, 2225 (1963).

15) W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y. (1966), p. 30.

16) M. S. Kharasch, J. L. Rowe and W. H. Urry, *J. Org. Chem.*, **16**, 905 (1951).

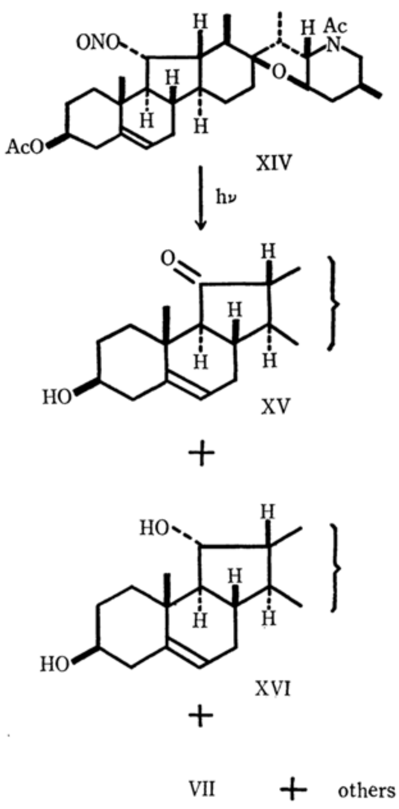
17) If these mechanisms operate, open-chain optically active secondary nitrites will produce racemic secondary alcohol on photolysis. The result of thermal decomposition of optically active 2-octyl nitrites in liquid phase (N. Kornblum and E. P. Oliveto, *J. Am. Chem. Soc.*, **71**, 266 (1949)) might be relevant at this point and we cited this in the preliminary communication.[1] However, since a recent investigation by Barton and co-workers demonstrated that the pyrolysis of nitrites in the molten state or solution may proceed *via* an ionic mechanism, this fact would not be relevant to the present argument. D. H. R. Barton, G. C. Ramsay and D. Wege, *J. Chem. Soc.*, (*C*), **1967**, 1915.

18) R. F. Zürcher, *Helv. Chim. Acta*, **46**, 2054 (1963). N. S. Bhacca and D. H. Williams, "Application of NMR Spectroscopy in Organic Chemistry," Holden-Day, San Francisco (1964), p. 13.

hydroxyl group in normal steroids. The difference in deshielding effects for the C-19 and C-18 methyls by the 11β-hydroxyl group is consistent with the results of the photolysis. The corresponding reaction in normal steroids, in which the 11β-hydroxyl group has almost the same deshielding effects (0.258 and 0.242 ppm) for the 19 and 18-methyl groups, leads to the formation of the oximino derivatives in both C-19 and C-18 methyls.[19] The correlation between the substituent effects and nitrite photolysis has recently been found in 3α,5α-cyclocholestan-6-ol nitrites.[20] It should be noted that in photolysis of VIIIb, the reaction which led to α-oximino-ketone (XIII) or 19-oximino derivative of 11β-ol (VIIIc) was not, at least, major. In the corresponding 11β-ol nitrite of the normal steroid having Δ^4-3-one, photolysis resulted in the formation of cyclopropane rings.[21]

In photolysis of 3-*O*,*N*-diacetyl-22,27-imino-17,23-oxidojerv-5-en-3β,11β-diol 11-nitrite (Ib) the formation of large amounts of 11-ketone (VII) together with 11α-ol (VI) would be rather distinctive. These can be produced before and (or) after epimerization *via* either disproportionation or α-hydrogen fission. Since a hydrogen on 11-carbon of this molecule is sterically very hindered, 11-ketone (VII) probably arises largely from α-hydrogen fission.[22]

Finally, photolysis of 3-*O*,*N*-diacetyl-22,27-imino-17,23-oxidojerv-5-ene-3β,11α-diol 11-nitrite (XIV), mp 146°C, which can be prepared quantitatively by nitrosation of the corresponding 11α-ol, is described. The irradiation of this compound in toluene for 3 hr led to a complex product mixture consisting of as many as 8 component as revealed by thin layer chromatography. 3-*O*,*N*-Diacetyl-22,27-imino-17,23-oxidojerv-5-en-3β-ol-11-one (VII) (7%), *N*-acetyl-22,27-imino-17,23-oxidojerv-5-en-3β-ol-11-one (XV) (8%), and a new compound melting at 279—281°C, (14%) could be separated by preparative thin layer chromatography. This compound was identified as *N*-acetyl-22,27-imino-17,23-oxidojerv-5-ene-3β,11α-diol (XVI) by direct comparison of its acetyl derivative with the corresponding 3-*O*,11-*O*,*N*-triacetyl derivative. Although it would appear that species generated from NO radical are playing a role in this facile deacetylation at 3 position, additional experimental work would be required before we could make any comments on this.



XIV

XV

XVI

VII + others

Experimental

Unless otherwise stated, infrared spectra were determined in Nujol using a Nihonbunko DS-402G type spectrophotometer or Jasco Model IR-E spectrophotometer. NMR spectra were determined on a Japan Electron Optics 3H-60 high resolution NMR spectrometer in deuteriochloroform solution using tetramethylsilane as an internal reference. The courses of reactions were followed by thin layer chromatography by using Wakogel B-5, unless stated otherwise.

3-*O*,*N*-Diacetyl-22,27-imino-17,23-oxidojerv-5-en-3β,11β-diol 11-Nitrite (Ib). This nitrite was prepared by nitrosation of 3-*O*,*N*-diacetyl-22,27-imino-17,23-oxidojerv-5-ene-3β,11β-diol in the usual way. The nitrite was recrystallized from chloroform-acetone mixture. Mp 209—210°C $[\alpha]_D+33.7°$ [*2] (*c* 1.9, chloroform). IR: ν_{max} 1734 (OAc), 1643 (N–Ac), 1725, 1621 (N–O), and 785 cm^{-1} (O–N). NMR: τ 8.95 C-19 methyl).

Found: C, 68.60; H, 8.50; N, 5.33%. Calcd for $C_{31}H_{46}O_6N_2$: C, 68.60; H, 8.54; N, 5.16%.

Photolysis of the Nitrite Ester Ib. The nitrite ester Ib (450 mg) in dry toluene (15 m*l*) under an atmosphere of dry nitrogen was irradiated with a 150-W high pressure mercury arc lamp for 3.5 hr. After evaporation of solvent, the residue was extracted with chloroform and the chloroform solution was washed with water. The residue (538 mg) gave 6 spots on thin

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[19] D. H. R. Barton and J. M. Beaton, *J. Am. Chem. Soc.*, **84**, 199 (1962).

[20] H. Suginome. T. Tsuneno and T. Masamune, *Tetrahedron Letters*, **1967**, 4605.

[21] D. H. R. Barton and J. M. Beaton, *J. Am. Chem. Soc.*, **83**, 4083 (1961).

[22] Although, in the preliminary communication,[1] we took the view that the formation of the 11-ketone (VII) might be attributed largely to disproportionation, this speculation might prove to be wrong on the basis of further experimental work.

[*2] In the preliminary communication, this was reported as $[\alpha]_D-30°$.

layer chromatogram. Among these spots, second, third and sixth spots from the highest one were very minor (Merck aluminum oxide G, type E was used after adding a further 5% of gypsum. A mixture of methanol and ether (1 : 50 vol%) was used as solvent). Preparative thin layer chromatography afforded the following amounts of residues corresponding to each band. The highest band, 103 mg (A), second band, 17 mg (B), third band, 26 mg (C), fourth band, 117 mg (D), fifth band, 61 mg (E). The residue (A) showed mp 210—212°C and was identical with authentic 11-ketone, (VII).[8] R_f value of the residue (B) corresponded to that of Ia. However, this did not afford crystalline material and it has not yet been possible to identify it. The residue (C) was also minor and could not be identified. The residue (D) showed mp 236—238°C and was identical with authentic 11*α*-ol (VI). The residue (E) (61 mg) was separated into two substances by preparative thin layer chromatography. One (22 mg) melted at 234.5—235°C and was 19-oximino derivative III. IR: ν_{max} 1735 (OAc), 1668 (N–Ac), 3406, and 3205 cm^{-1} (OH). NMR: τ 2.35 (methine at C-19).

Found: C, 68.48; H, 8.47; N, 5.18%. Calcd for $C_{31}H_{46}O_6N_2$: C, 68.60; H, 8.54; N, 5.16%.

The other (5 mg) melted at 197—200°C and has not been identified.

***N*-Acetyl-22,27-imino-17,23-oxidojerv-4-en-11*β*-ol-3-one (VIIIC).** 22,27-Imino-17,23-oxidojervan-4-en-11*β*-ol-3-one (500 mg) was dissolved in 22 m*l* of pyridine and 17 m*l* of acetic anhydride and set aside for 1.5 hr at room temperature. After work-up as usual chloroform-acetone solution of the residue yielded crystals of the *N*-acetyl derivative. 450 mg mp 240—242°C. IR: ν_{max} 1625 (N–Ac), 1652 (*α*,*β*-unsaturated ketone), and 3458 cm^{-1} (OH). NMR: τ 8.59 (C-19 methyl), τ 7.90 (*N*-acetyl) and τ 4.31 (C-4H).

Found: C, 73.86; H, 9.28; N, 2.84%. Calcd for $C_{29}H_{43}O_4N$: C, 74.16; H, 9.23; N, 2.98%.

***N*-Acetyl-22,27-imino-17,23-oxidojerv-4-en-11*β*-ol-3-one 11-Nitrite (VIIIb).** *N*-Acetyl-22,27-imino-17,23-oxidojerv-3-en-11*β*-ol-3-one (300 mg) in pyridine (5m*l*) was cooled to −20—−30°C. To this solution there was added dropwise nitrosyl chloride-pyridine mixture while stirring until the solution turned brown. The solution was further stirred for 20 min and was poured into water. Resultant precipitates were collected, dried and recrystallized from acetone-ether. Mp 175—180°C $[\alpha]_D+186.2°$ (*c* 0.73, chloroform). IR: ν_{max} 1696 (*α*,*β*-unsaturated ketone), and 1662 cm^{-1} (N–Ac). NMR: τ 8.82 (C-19 methyl) and τ 7.95 (*N*-acetyl).

Found: C, 69.70; H, 8.68; N, 5.28%. Calcd for $C_{29}H_{42}O_5N_2$: C, 69.85; H, 8.49; N, 5.62%.

Photolysis of the Nitrite Ester VIIIb. The nitrite ester (828 mg) in dry toluene (13 m*l*) at room temperature and under an atmosphere of dry nitrogen was irradiated with 150-W high pressure mercury arc lamp for 2 hr. After removal of the solvent, the residue was extracted with chloroform. The chloroform solution was washed with water and dried over anhydrous sodium sulfate. The residue was a complex mixture and revealed at least 8 spots on thin layer chromatogram. The preparative thin layer chromatography (Wakogel B5) was carried out as follows: the reaction product was twice developed with a mixture of methanol and ether (1 : 15 vol%). The highest band (least polar compound) afforded the residue (82 mg). This was again purified by thin layer chromatography (solvent: ether), yielding crystals of IX, (16 mg), mp 223—225°C (acetone-ether). $[\alpha]_D+94°$ (*c*, 1.5, chloroform). IR: ν_{max} 1652 (*α*,*β*-unsaturated ketone), 1729 (5-membered ketone), and 1642 cm^{-1} (N–Ac). NMR: τ 8.81 (C-19 methyl) and τ 7.88 (*N*-acetyl).

Found: C, 74.06; H, 9.00; N, 2.89%. Calcd for $C_{29}H_{41}O_4N$: C, 74.48; H, 8.84; N, 3.00%.

The second band which was major one was eluted to afford oil (120 mg) from which crystals (106 mg) were obtained. This was identical with 11*β*-ol (VIIIc). All but the above two bands were eluted and combined. The residue was developed twice with methanol and ether (1 : 10 vol%). The least polar compound (11 mg) melted at 249—252°C (acetone-ether). This was identified as 11*α*-ol (XIa) by comparison with the substance synthesized as below. $[\alpha]_D +93°$ (*c* 2.0, chloroform). IR: ν_{max} 1653 (*α*,*β*-unsaturated ketone), 3432 (OH), and 1642 cm^{-1} (N–Ac). NMR: τ 8.86 (C-19 methyl) and τ 7.89 (*N*-acetyl).

Found: C, 74.01; H, 9.20; N, 3.18%. $C_{29}H_{43}O_4N$: C, 74.16; H, 9.23; N, 2.98%.

The NMR spectrum of the crude substance obtained from the rest of the bands above revealed an absence of signals due to a methine proton on carbon bearing an oximino function.

***N*-Acetyl-22,27-imino-17,23-oxidojerv-4-en-11*α*-ol-3-one (XI).** 11-*O*,*N*-Diacetyl-22,27-imino-17,23-oxidojerv-4-en-11*α*-ol-3-one (20 mg) in 5% aqueous ethanolic potassium hydroxide (10 m*l*) was refluxed for 40 min. After removal of the solvent, the residue was extracted with chloroforom and water. From the chloroform layer, 11*α*-ol (8 mg) was obtained. Mp 249—252°C (acetone-ether). This was identical with the product obtained from the photolysis above.

***N*-Acetyl-22,27-imino-17,23-oxidojerv-4-en-3,11-dione (IX).** a) To 22,27-imino-17,23-oxidojerv-4-en-11*β*-ol-3-one (100 mg) and chromic anhydride (150 mg) in dimethylformamide (11 m*l*), there was added 3 drops of concentrated sulfuric acid and the mixture was stirred for 44 hr at room temperature. After decomposition of the excess chromic anhydride with aqueous saturated sodium bisulfite, tetrahydrofuran was added to the solution and the solution was filtered. Acetone was added to the residue obtained and the solution was again filtered. Removal of the solvent and the extraction of the residue with chloroform yielded crude diketone which was purified by preparative thin layer chromatography to yield amorphous 22,27-imino-17,23-oxidojerv-4-ene-3,11-dione (70mg). IR: ν_{max} 1730 (5-membered ketone), 1667 (*α*,*β*-unsaturated ketone), and 3441 cm^{-1} (NH). NMR: τ 8.80 (C-19 methyl).

Found: C, 73.83; H, 9.21; N, 3.04%. Calcd for $C_{29}H_{41}O_4N$: C, 74.48; H, 8.84; N, 3.00%.

This (30 mg) was acetylated in the usual way to yield *N*-acetyl-22, 27-imino-17, 23-oxidojerv-4-ene-3, 11-dione (18 mg), Mp 223—225°C. This was identical with the product obtained from the photolysis above. b) *N*-Acetyl-22,27-imino-17,23-oxidojerv-4-en-11*α*-ol-3-one (50 mg), chromic anhydride (50m g) and two drops of concentrated sulfuric acid in dimethylformamide (7 m*l*) were stirred for 44 hr at room temperature. After work-up as in the case of the procedure a) above, the residue was purified by preparative thin layer chromatography to yield diketone IX (20 mg). Mp 223—225°C. This was identical with the specimen obtained by a) above.

3-*O*, *N*-Diacetyl-22, 27-imino-17, 23-oxidojerv-5-en-3*β*,11*α*-diol 11-Nitrite (XIV). VI in pyridine was nitrosated at −30°C in usual way. The product was recrystallized from acetone-ether. Mp 146°C.

Found: C, 69.17; H, 8.86; N, 5.00%. Calcd for $C_{31}H_{46}O_6N_2$: C, 68.60; H, 8.54; N, 5.16%.

IR: ν_{max} 1731 (OAc), 1633 (N–Ac), 1644 (N–O), 764, and 777 cm^{-1} (O–N); NMR: τ 8.82 (C-19 methyl).

Photolysis of the Nitrite XIV. The nitrite above (450 mg) in dry toluene (15 m*l*) was irradiated under dry nitrogen at room temperature for 3 hr. After removal of the solvent under reduced pressure, the residue was extracted with chloroform. After usual work-up, the residue (556 mg) obtained was a complex mixture and at least 8 spots were observed on thin layer chromatogram. The three major compounds were isolated by preparative thin layer chromatography (Merck, aluminum oxide G, gypsum content 15%) as follows:

The reaction product was developed with ether. The highest band (least polar compound) afforded the residue (48 mg) from which pure 11-ketone, (VII), mp 210—212°C (from acetone), 30 mg, was obtained. Products from the second and third bands were minor and could not be identified. The residues from the fourth and fifth bands (172 mg) were combined and developed again. The fourth band afforded 42 mg of oily residue. Recrystallization from ether afforded 30 mg of crystals (mp 188°C) which was identified as *N*-acetyl-22,27-imino-17,23-oxidojerv-5-en-3*β*-ol-11-one, (XV). The residue (65 mg) from the fifth band afforded crystals of 54 mg, mp 279—281°C (from acetone), which was shown to be *N*-acetyl-22,27-imino-17,23-oxidojerv-5-ene-3*β*,11*α*-diol (XVI) by converting it into the diacetyl derivative. IR: ν_{max} 1647 (N–Ac) and 1677 cm^{-1} (trisubstituted double bond). NMR: τ 7.89 (N–Ac) and τ 8.98 (C-19 methyl).

Found: C, 73.43; H, 9.41; N, 2.77%. Calcd for $C_{29}H_{45}O_4N$: C, 73.84; H, 9.62; N, 2.97%.

Acetylation of *N*-Acetyl-22,27-imino-17,23-oxidojerv-5-en-3*β*,11*α*-diol. Photoproduct XVI was acetylated in usual way. The acetylated product was identical with 3-*O*,11-*O*,*N*-triacetyl-22,27-imino-17,23-oxidojerv-5-ene-3*β*,11*α*-diol in every respect.

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