A New Photochemical Fragmentation of Nitrogen Heterocycles

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WE report that certain steroidal alkaloid nitrite esters substituted vicinally by a nitrogen moiety undergo carbon–carbon fission on irradiation.

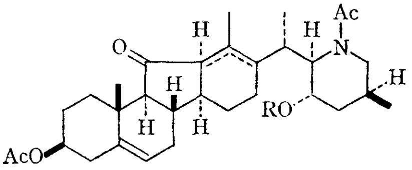
3β,23α-Dihydroxy-22,27-imino-11-oxojerva-5,-13(17)-diene 3,*N*-diacetate (Ia), which was prepared by Birch reduction of jervine[1] followed by partial acetylation, was converted by treatment with nitrosyl chloride in pyridine[2] into the corresponding unstable nitrite (Ib). Photolysis of a benzene solution of (Ib) for 1 hr. by a 150 w high-pressure mercury arc lamp under the conditions commonly used for the Barton reaction[3] gave a 33% yield of a single product (II), m.p. 150—152°, after chromatography on silicic acid.

The following evidence clearly indicated the compound to have the structure (II). Elemental analysis and mass spectrometry (M^+ 384) indicated the formula $C_{24}H_{32}O_4$, corresponding to the loss of the nitrogen moiety in (Ia). In the n.m.r. spectrum of (Ia), signals due to *N*-acetyl, acetoxyl, and 18- and 19-methyl groups appeared as singlets at τ8·00, 8·03, 8·15, and 9·03 respectively, and those due to 21- and 26-methyl groups as a coincident broad doublet centred at τ8·83 ($J = 6·6$), but the n.m.r. spectrum of (II) retained only three singlets at τ7·99, 8·16, and 9·05 which are attributable to aectoxyl and 18- and 19-methyl groups. A doublet in (Ia) was also retained in the spectrum of (II), being centred at τ8·83 ($J = 6·6$). However, intensity of a doublet in (II) was just a half of that of the corresponding doublet of (Ia), proving that either the 21-methyl or the 26-methyl was removed from (Ia). Moreover, the n.m.r. spectrum of (II) showed the presence of aldehydic proton as a doublet centred at τ0·56 ($J = 4·2$). A notable feature of the i.r. spectrum of the product was the absence of a band due to an *N*-acetyl group and the presence of typical aldehyde bands[4] at 2697, 2799, and 1740 cm.$^{-1}$ (shoulder). Only the structure (II) accommodates the spectral data and the molecular formula above.

In a similar manner, nitrite (IIIb) which can be prepared by partial acetylation of 3β,23α-dihydroxy-22,27-imino-11-oxojerva-5,12-diene *N*-acetate followed by nitrosation gave rise to the corresponding aldehyde (IV), m.p. 167—171°, in 13% yield. Its spectroscopic properties were in complete accord with the assigned structure.

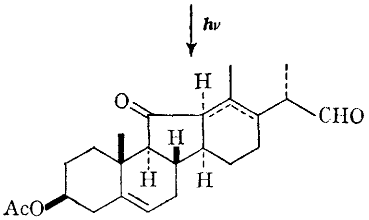
The course of this reaction apparently involves the formation of the imino-intermediates (VII) followed by acid hydrolysis during separation by chromatography on silicic acid. The following sequence (V—VIII) may be proposed for this photochemical fragmentation.

As we have observed the formation of amines in a study of a simpler system, *i.e.*, *N*-acetyl-3-hydroxy-5-methylpiperidine nitrite, it is very probable that the reaction proceeds mainly by rupture of the nitrogen–acyl linkage as indicated.[5]

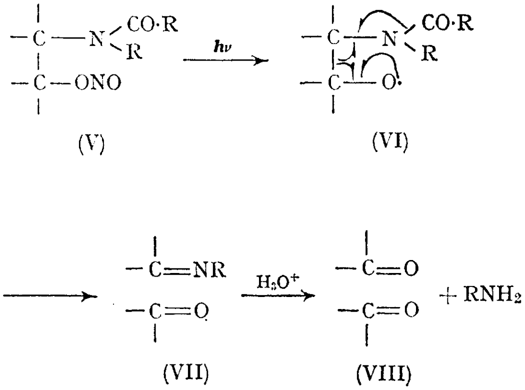


(I) a; R = H (13–17 double bond)
b; R = NO (13–17 double bond)

(III) a; R = H (12–13 double bond)
b; R = NO (12–13 double bond)



(II) (13–17 double bond) (IV) (12–13 double bond)



The present fragmentation reaction has a formal resemblance to the reactions observed by Barton and his co-workers in the photolysis of nitrite esters[6] bearing oxygen functions at the α-position in the pregnane series. The reaction may provide a useful synthetic route to certain aldehydes which are inaccessible by other procedures.[7]

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[7] *Cf.* R. W. Franck and W. S. Johnson, *Tetrahedron Letters*, 1963, 545.