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A FACILE RING CONTRACTION OF WIDDROL INVOLVING PHOTOLYSIS OF THE NITRITE ESTER [1]

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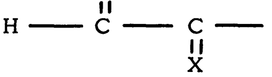
A facile three-step ring contraction of sesquiterpene widdrol (1) is described. The steps involve the first known example of the photoreaction of a 7-membered cyclic homoallyl alcohol nitrite to afford four isomeric α,β-unsaturated oximes (3), (4), (5) and (6).

In previous papers, several reactions involving homoallyl alkoxyl radicals generated photochemically or thermally from cyclic alcohol nitrites and hypoiodites were reported.[2] In this paper, we wish to report the three-step ring contraction of sesquiterpene widdrol (1) [3] which involves the first known example of the photoreaction of a 7-membered cyclic homoallyl alcohol nitrite.

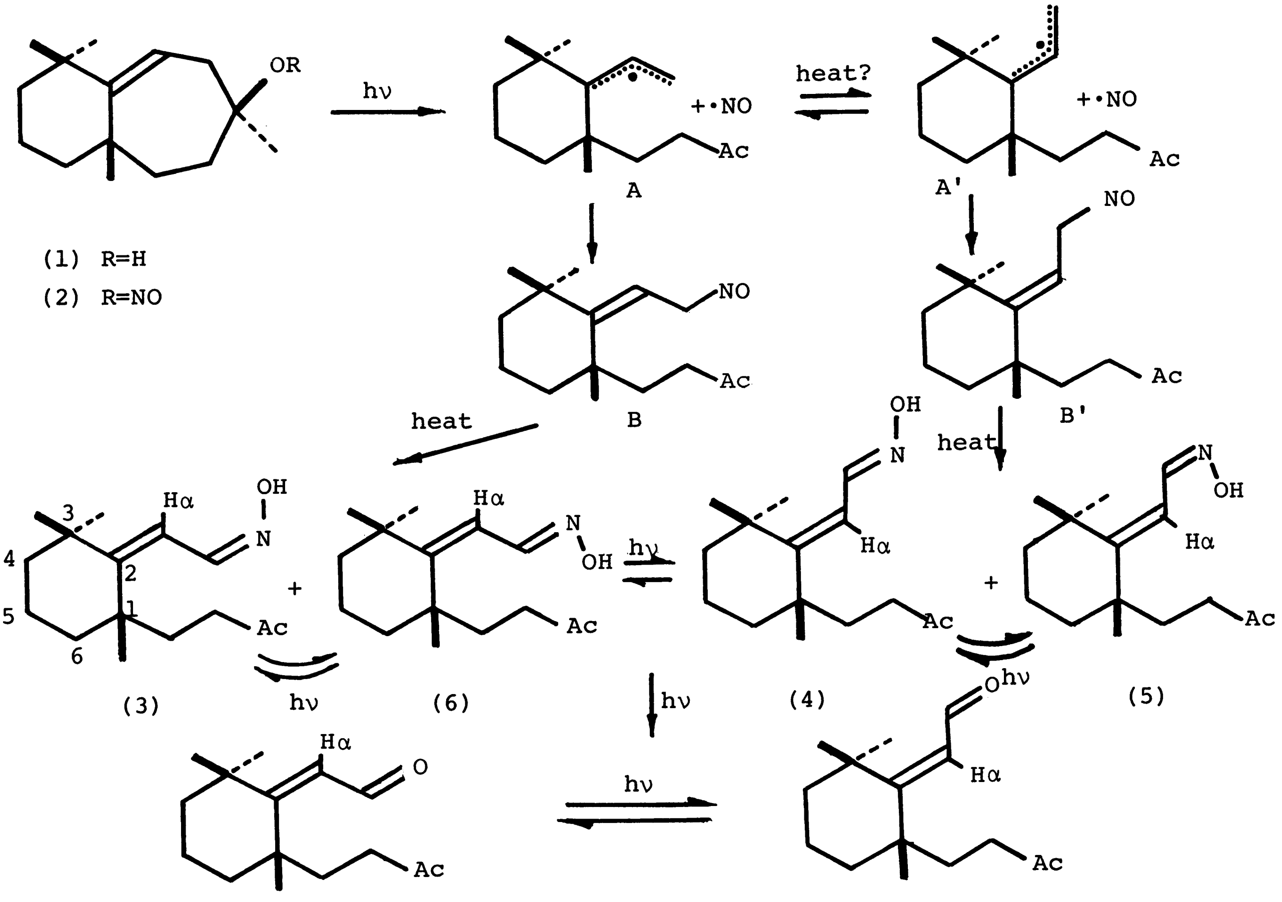
Irradiation of an oily widdrol nitrite ester (2) (1 g), prepared from widdrol by the usual method, in dry benzene (100 ml) through Pyrex with a 100-W high pressure Hg arc lamp for 45 min resulted in a mixture of several products. Silica gel chromatography of the combined products from five experiments afforded an oxime (3) (0.8 g), an oily 2 : 1 mixture of two oximes (4) and (5) (2.0 g), an oxime (6) (1.9 g), and an oily 1 : 5 mixture of two α,β-unsaturated aldehydes (7) and (8) (0.09 g) in the order of decreasing polarities. The molecular formula of the oximes (3) and (6) was shown to be $C_{15}H_{25}O_2N$ (Mass. m/e 251, $M^{\dot{+}}$) and the oximes (4) and (5) were also proved to be geometrical isomers of the former, on the basis of the spectral analysis. In the n.m.r. spectra of all the oximes (3), (4), (5) and (6), a pair of doublets due to isolated vicinal olefinic protons of the transoid systems



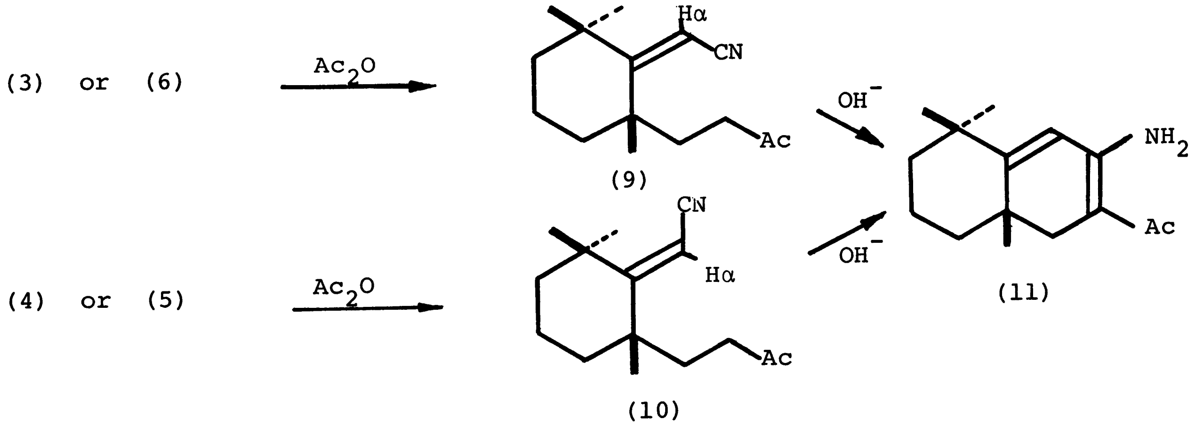
$\mathrm{H{-}\overset{\|}{C}{-}\underset{\underset{X}{\|}}{C}{-}H}$ and a 3-proton singlet due to an acetyl group were present.

[n.m.r. 60MHz, $CDCl_3$, TMS, τ, Hz. (3) α-H, d, 3.29, J=9.0, -CH=N-, d, J=9.0, acetyl, S, 7.88; (4) α-H, d, 4.05, J=10.2, -CH=N-, d, 1.62, J=10.2, acetyl, S, 7.87; (5) α-H, d, 3.50, d, J=9.0, -CH=N-, d, 2.32, J=9.0, acetyl, S, 7.87; (6) α-H, d, 3.80, J=10.2, -CH=N-, d, 1.70, J=10.2, acetyl, S, 7.86]

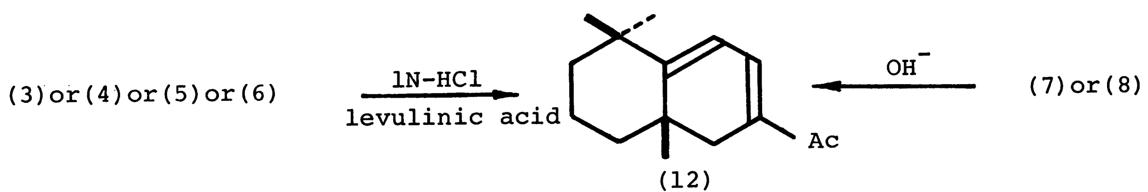
All the oximes exhibited a series of bands due to the acetyl group and the α,β-unsaturated aldoxime group in their i.r. spectra and intense absorptions due to an α,β-unsaturated aldoxime group in their u.v. spectra. These spectral properties together with the modes of the photochemical breakdown of the nitrite can



Scheme 1



Scheme 2



Scheme 3

be interpreted in terms of the four formulae given in Scheme 1 with the exceptions of the geometries of the conjugated system and the hydroximino group which were assigned in the following manner.

In refluxing acetic anhydride for 3 hr the oxime (3) or (6) was dehydrated to an identical oily nitrile (9) (n.m.r. α-H, S, τ4.52, acetyl, S, 7.84) in 80 % yield. Treatment of the oxime (4) or (5) under the same conditions produced another isomeric nitrile (10) (n.m.r. α-H, S, τ4.75, acetyl, S, 7.87) in 75 % yield. Thus, it was confirmed that the geometries of the hydroximino substituent attached to the Δ^2-double bond of (3) and (6) and those of (4) and (5) are different. The nitrile (9) in refluxing 30 % aq. ethanolic KOH for 2 hr gave an aminoketone (11), m.p. 166-168°C, (n.m.r. 4-H, S, τ4.31, acetyl, S, 7.88) as a single product. Treatment of the nitrile (10) under the same conditions, however, afforded (11) in only 5 % yield, which was confirmed by g.l.c. analysis. The difference in the rates of transformation of the nitriles (9) and (10) indicated that the $C\equiv N$ substituent and the 1,2 bond lie on the same side in the nitrile (9) [(*Z*)-nitrile] and on opposite sides in the nitrile (10) [(*E*)-nitrile]. The establishment of the geometries of these nitriles led us to conclude that the geometries of the conjugated double bonds of the four oximes are as depicted in Scheme 1. *Cis-trans* isomerism of the four oximes was solved by n.m.r. spectroscopy. In the oximes (3) and (5), the protons Hα appeared downfield from the corresponding protons of the oximes (6) and (4) by 0.51 and 0.55 ppm and therefore the hydroxyl groups and the α-protons in the oximes (3) and (5) lie on the same side [(*Z*)-oximes] and those in the oximes (4) and (6) lie on opposite sides[4] [(*E*)-oximes].

The i.r., n.m.r., and u.v. spectra of the mixture of the compounds (7) and (8) [νmax 1720 cm^{-1}, 1664 cm^{-1} and 1595 cm^{-1}; n.m.r., (7) α-H, d, τ3.96, formyl-H, d, -0.25 (J=7.8 Hz), acetyl, S, 7.87; (8) α-H, d, 4.17, formyl-H, d, -0.36 (J=8.0 Hz), acetyl, S, 7.87] indicated that the structures of (7) and (8) should be formulated as depicted in Scheme 1.[5] Treatment of any of the four oximes (3), (4), (5) and (6) with 1N-hydrochloric acid and levulinic acid[6] at 90° for 1 hr afforded a methylketone (12) in 70 % yield. The structure was confirmed to be 2-acetyl-5,5,9β-trimethyl-$\Delta^{2,4}$-hexahydro-3-naphthalene (12) (n.m.r. 3-H, q, J=6.0 and τ3.0, 3.14, 4H, d, J=6.0, acetyl, S, 7.70) based on the various spectra. The α,β-unsaturated ketone in refluxing 30 % aq. ethanolic KOH solution for 30 min. also gave (12) in 55 % yield. Thus, a very facile ring contraction of widdrol to (12) was achieved in three steps by exploiting the nitrite photolysis.

Pathways involving thermal isomerization of an allyl radical A to A'[7], depicted in Scheme 1, might account for the formations of the photoproducts. However, the formation of the oximes (4) and (5) *via* photochemical isomerization of the oximes (3) and (6) is more probable for the reasons that (1) simple allyl radicals are remarkably stable toward geometrical isomerization[8] and (2) the formation of the two ketones (7) and (8) seems to be an indication of the involvement of excited species of the oximes in the reaction[9] although the photolysis was carried out with a Pyrex-filtered light.

References and Notes

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