

THE CYCLIC ADDITION OF ALKOXYL RADICALS

I. CYCLIC ADDITIONS OF 4-PENTENOXYL RADICAL

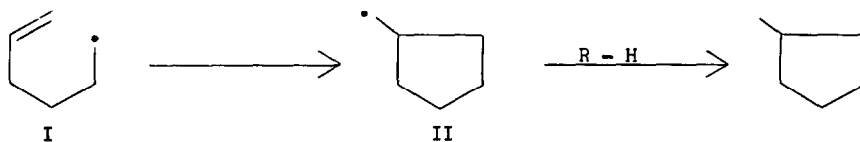
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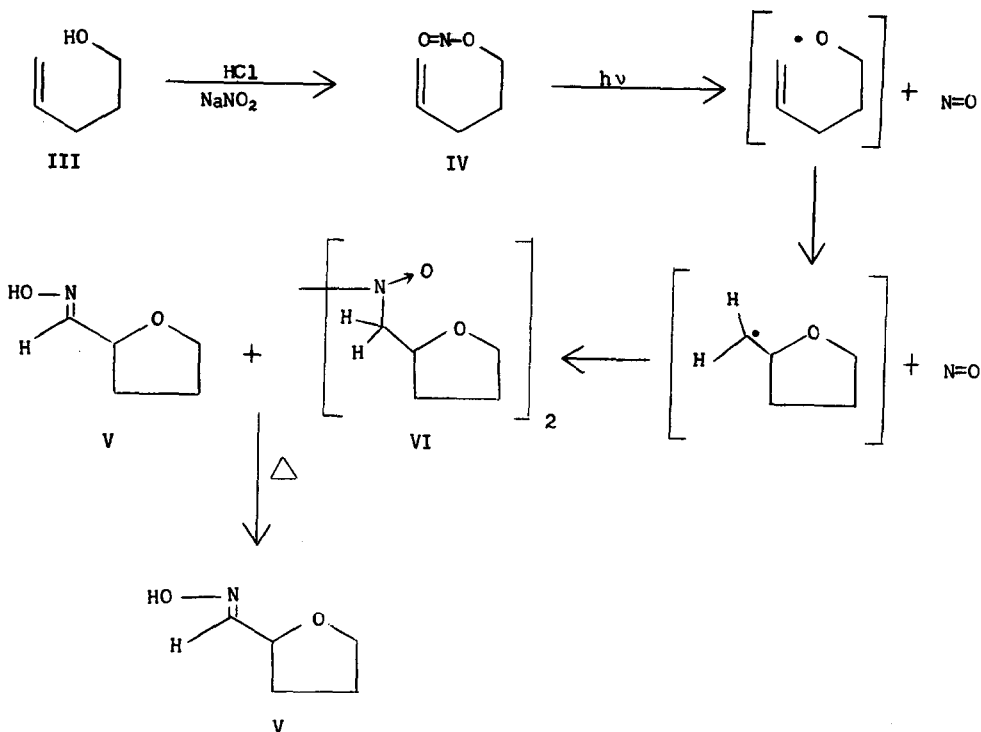
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A number of recent papers have reported on the cyclic additions of a variety of carbon radicals and the variation in the resulting ring size.² The 5-hexenyl radical (I) has been reported to close to a five-membered ring (II), yielding a primary radical, rather than to close to a six-membered ring and give the thermodynamically more stable secondary radical.²



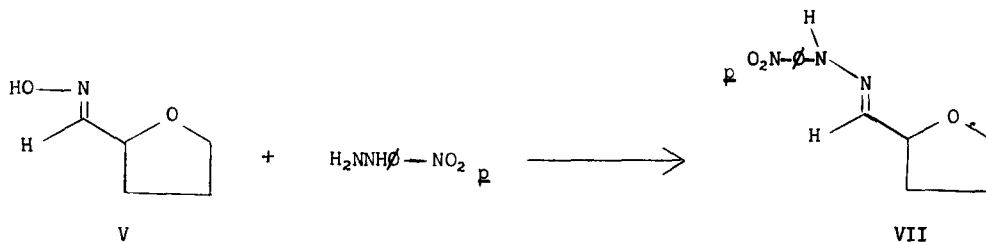
We would like to report some of our preliminary findings on the cyclization of alkoxy radicals. Our initial studies have concentrated on the 4-pentenoxy radical. We have been generating our alkoxy radicals by photolyzing nitrite esters. Interestingly, this alkoxy radical also cyclizes via a five-membered transition state to give the thermodynamically less stable primary radical.

We have found a convenient method of preparation of our nitrite esters in a variation of the method of Hunter and Marriott.³ By adding hydrochloric acid dropwise to the two-phase mixture of 4-penten-1-ol (III) and aqueous sodium nitrite at 0° C high yields of the nitrite ester (IV), free from complicating side reactions, were obtained. The terminal double bond of the alcohol (III) had not isomerized during the ester formation as indicated by NMR.



Solutions of the nitrite ester in benzene under a nitrogen atmosphere were irradiated using a medium pressure mercury lamp with a pyrex filter. The photolysis was complete within forty-five minutes as indicated by the absence of the nitrite ester peak in the UV spectrum.⁴ The benzene was stripped off, leaving a mixture of the oxime (V) and nitroso dimer (VI). This mixture was heated at 45° C for fourteen hours in order to cleave all the nitroso dimer and isomerize it to the oxime (V). The tetrahydrofurfural oxime was then isolated by chromatographing the mixture on a column of Florisil activated at 500° F with chloroform as eluent. The structure of the oxime is based on the following physical and chemical data. The infrared spectrum of V indicated an oxime with bands at 3.0 μ and 6.25 μ . The mass spectrum showed V to be isomeric with starting material with a molecular

ion at m/e 115. The NMR spectrum was the most definitive, with the oxime proton appearing at 0.5τ (1H). This peak was split into two peaks of relative intensity 3 to 7 when the spectrum was run in DMSO; this is due to the syn and anti isomers. The trigonal carbon proton appeared as a doublet at 2.75τ ($J = 7$ cps, 0.7 H) and a doublet at 3.3τ ($J = 5$ cps, 0.3 H); this also is due to the syn and anti isomers. The protons at carbons 2 and 5 appeared as a multiplet at 5.9τ (3H) and the protons at carbons 3 and 4 appeared as a multiplet at 8.3τ (4H). Final proof of the structure of V was its conversion to VII by stirring it with p-nitrophenylhydrazine in acetic acid. Compound VII had the same melting point as that reported in the literature.⁵



The highest yield of V (68% yield) was obtained when a 7.5×10^{-2} M solution of nitrite ester (IV) was photolyzed. At this concentration, five other products in low yields were observed; we will report on their structures later. Two of the other isomers (total 14% yield) were shown to be not monomeric by mass spectral analysis.

Thus it appears that the majority of the 4-pentenoxyl radicals cyclize to a five-membered ring; this is similar to the carbon radical case. This is also interesting in light of the fact that the Barton Reaction requires a six-membered transition state.⁶ One possible explanation for this observation is that entropy factors are governing the mode of cyclization.⁷

We are actively studying the cyclization of other alkoxy radicals and various mechanistic considerations; these will be reported at a later date.

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