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AN UNUSUAL CLEAVAGE OF A CYCLIC SECONDARY HYDROPEROXIDE: FORMATION OF 6-ACETOXYOCTA-2,7-DIENAL

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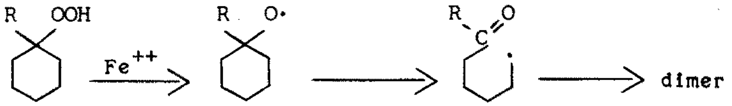
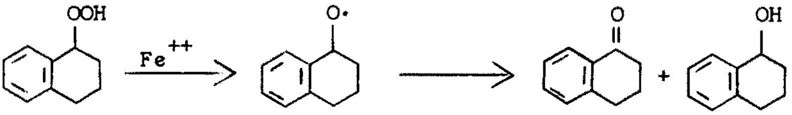
The reaction of cyclic tertiary hydroperoxides with ferrous salts has been shown to produce alkoxy radicals.(1) In the absence of suitable hydrogen donors, cleavage reactions occur predominantly,(2) as in equation 1. For secondary cyclic hydroperoxides (equation 2), cleavage is not the major reaction path,(3,4) and even in the presence of excellent hydrogen donors,(4) large



(1)

R = OH, alkyl



(2)

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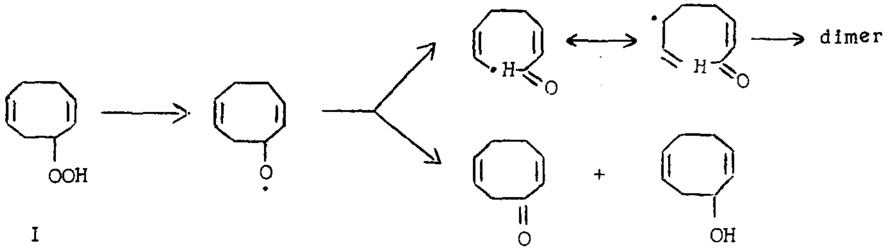
amounts of the cyclic ketone result. It seemed possible that the cleavage reaction for cyclic secondary hydroperoxides might be more competitive if the radical resulting from carbon-carbon bond breaking were an allylic one. Thus, for the hydroperoxide I, reaction <u>via</u> 3a might compete successfully with the more usual reaction path, 3b.

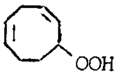


I

(3a

(3b

The hydroperoxide (I) was available from the liquid-phase oxidation of <u>cis,cis</u>-1,5-cyclooctadiene at 60°C. Separation of I (and its double bond isomer II) from the crude oxidate was accomplished by extraction with 5:1 petroleum ether-benzene solvent, in which I and II were soluble, but polyperoxides were not. The



II

hydroperoxide mixture could be converted to cyclooctanone (identified as the semicarbazone, m.p. and mixed m.p. 169-170°) either by hydrogenation to cyclooctanol and dichromate oxidation or dehydration to a mixture of α,β-unsaturated ketones followed by hydrogenation. The assignment of structure I to the major component is described in an accompanying paper.(5)

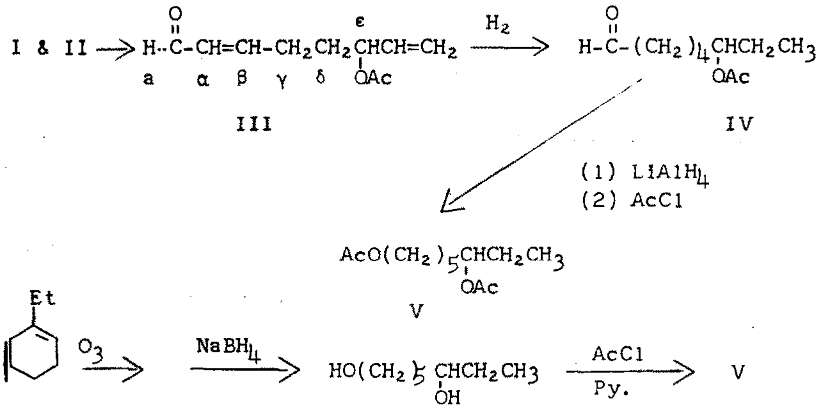
When a solution of the hydroperoxide mixture in 50% aqueous isopropanol was added to an aqueous suspension of ferrous sulfate heptahydrate, there was obtained an oil which contained an aldehyde function as determined by IR and NMR. Evaporative distillation at 50° and .002 mm. removed ketone and alcohol; the aldehyde portion (ca. 40% of the product) remained as a non-volatile residue. That the aldehyde was α,β-unsaturated was established by IR, NMR and UV (λ_{max} 222mμ; ϵ_{max} 6,400, isooctane). Although the aldehyde could be hydrogenated and oxidized to saturated acid, little detailed structural information was obtained.

The intermediate allyl radical was trapped with cupric acetate which transferred an acetate ligand predominantly to the internal position.(6) A solution of I and II in acetic acid was added simultaneously with an aqueous solution of ferrous sulfate to a well-stirred solution of cupric acetate in acetic acid. This product also showed evidence of an α,β-unsaturated aldehyde, but in this instance, the aldehyde was distillable. Several fractions were obtained on distillation of 10.5 g. of product as shown in Table I.

TABLE I

Fraction No.	b.p. at .3 mm.	Wt. (g.)	Structural Features
1	31-50	3.26	Predominantly α,β-unsaturated ketones and alcohols
2	50-63.5	.71	Some aldehyde and O-H functions
3	63.5-80	3.57	α,β-Unsaturated aldehyde acetat
4	Non-volatile	2.36	

The NMR spectrum of fraction 3 revealed two aldehyde doublets at -0.3τ and 0.55τ and a complex group of eleven peaks centered at ca. 3.2τ. Treatment of the mixture with iodine at room temperature caused the disappearance of the low-field aldehyde doublet along with half of the peaks at 3.2τ. What remained could be accomodated nicely by the aldehyde-acetate III with trans stereochemistry about the double bond: H_a, 0.55τ, doublet, $J_{a\alpha} = 7.5$ cps; H_α, 3.9τ, multiplet, $J_{a\alpha} = 7.5$ cps, $J_{\alpha\beta} = 15.5$ cps (trans); H_β, 3.14τ, double triplet, $J_{\alpha\beta} = 15.5$ cps (trans), $J_{\beta\gamma} = 5.8$ cps.(7) The remainder of the NMR spectrum showed a very complex multiplet at 3.8-5.0τ consisting of the three vinyl hydrogens and H_ϵ, H_γ at 7.6τ, H_δ at 8.1τ and the acetate-methyl singlet at 8.00τ. Confirmation of the vinyl group was obtained from the infrared spectrum of III which exhibited strong bands at 985 cm.$^{-1}$ and 932 cm.$^{-1}$, characteristic of the $-CH(OCOR)CH{=}CH_2$ grouping.(8) This shift of the low-frequency vinyl absorption from 910 cm.$^{-1}$ to 932 cm.$^{-1}$ requires a polar group (the acetate function) on the carbon atom adjacent to the double bond.(8)



$$\text{I \& II} \longrightarrow \underset{a}{H}-\overset{O}{\overset{\|}{C}}-\underset{\alpha}{CH}=\underset{\beta}{CH}-\underset{\gamma}{CH_2}\underset{\delta}{CH_2}\overset{\epsilon}{\underset{OAc}{CH}}CH=CH_2 \xrightarrow{H_2} H-\overset{O}{\overset{\|}{C}}-(CH_2)_4\underset{OAc}{CH}CH_2CH_3$$

III IV

$$\xrightarrow[(2)\ AcCl]{(1)\ LiAlH_4} AcO(CH_2)_5\underset{OAc}{CH}CH_2CH_3 \qquad (4)$$

V

$$\xrightarrow{O_3}\ \xrightarrow{NaBH_4} HO(CH_2)_5\underset{OH}{CH}CH_2CH_3 \xrightarrow[Py.]{AcCl} V \qquad (5)$$

The aldehyde responsible for the low-field aldehyde doublet, the minor constituent of the aldehyde mixture, is undoubtedly <u>cis</u>-III: H_a, 0.3τ, doublet, $J_{a\alpha} = 7.8$ cps; H_α, 4.1τ, multiplet, $J_{a\alpha} = 7.8$ cps, $J_{\alpha\beta} = 11.2$ cps (<u>cis</u>); H_β, 3.4τ, double triplet, $J_{\alpha\beta} = 11.2$ cps, $J_{\beta\gamma} = 8.0$ cps. The remainder of the spectrum is similar to <u>trans</u>-III. Hydrogenation of either <u>cis</u>- or <u>trans</u>-III in ethyl acetate solution with palladium-on-carbon catalyst gave the same aldehyde, IV. The position of the acetate function could be assigned rigorously to C_6 of IV by the well-resolved pattern of the methyl triplet in the NMR spectrum.(9) Reduction of IV with lithium aluminum hydride followed by acetylation gave 1,6-diacetoxyoctane (V), identical in infrared spectrum and GPC retention time with material prepared by reductive ozonolysis(10) of 1-ethylcyclohexene. These reactions are outlined in equations 4 and 5.

Formation of III via equation 3a should give the <u>cis</u> isomer exclusively. In fact, if the reaction is conducted in a non-acidic medium such as aqueous acetonitrile or isopropanol, the <u>cis</u> isomer is formed predominantly. Also, the dimeric aldehyde formed in the absence of cupric salts is exclusively <u>cis</u>: H_a, 0.1τ, $J_{\alpha\beta} = 11$ cps. It is probable, therefore, that in the reaction in acetic acid solvent, the unstable <u>cis</u> isomer is formed initially and slowly rearranges to the <u>trans</u> product.

REFERENCES

1. A.G. Davies, *Organic Peroxides*, Butterworths, London, 1961, p. 174; R.S. Orr and H.L. Williams, *J. Am. Chem. Soc.*, *78* 3273 (1956).

2. N. Brown, M.S. Hartig, M.J. Roedel, A.W. Anderson and C.E. Schweitzer, *J. Am. Chem. Soc.*, *77*, 1756 (1955); M.S. Kharasch, F.J. Arimoto and W. Nudenberg, *J. Org. Chem.*, *16*, 1556 (1951); D.D. Coffmann and H.N. Cripps, *J. Am. Chem. Soc.*, *80*, 2877 (1958).

3. A. Robertson and W.A. Waters, *J. Chem. Soc.*, 1578 (1948); W. Pritzkow and K.A. Muller, *Ber.*, *89*, 2321 (1956); W. Pritzkow and I. Hahn, *J. prakt. Chem.*, [4], *16*, 287 (1962).

4. M.S. Kharasch, A. Fono and W. Nudenberg, *J. Org. Chem.*, *15*, 763 (1950).

5. W.J. Farrissey, Jr., R.H. Perry, Jr., F.C. Stehling and N.F. Chamberlain, *Tetrahedron Letters*,

6. J. Kumamoto, H.E. De LaMare and F.F. Rust, *J. Am. Chem. Soc.*, *82*, 1935 (1960); J.K. Kochi, *ibid.*, *83*, 3162 (1961); J.B. Braunwarth and G.W. Crosby, *J. Org. Chem.*, *27*, 2064 (1962).

7. R. Anet, *Tetrahedron Letters*, No. 20, p. 720 (1961), reports H_a, doublet, 0.27 , J, 7.2 cps; and $J_{\alpha\beta}$, 14.1 cps for a similar *trans*-α,β-unsaturated aldehyde.

8. L.J. Bellamy, *The Infra-red Spectra of Complex Molecules*, J. Wiley, New York, 1958, p. 49.

9. K.W. Bartz and N.F. Chamberlain, to be published. The author is indebted to N.F. Chamberlain for much of the NMR spectral interpretations.

10. J.A. Sousa and A.L. Bluhm, *J. Org. Chem.*, *25*, 108 (1960).