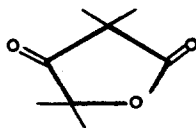


OXIDATION REACTIONS IN CONCENTRATED HYDROGEN PEROXIDE MEDIA

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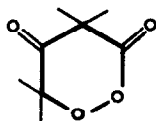
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Reactions of cyclobutanones with hydrogen peroxide and acid in which Baeyer-Villiger oxidation occurs have been reported to provide butyrolactones in good yields.¹ We have examined the behavior of tetramethyl-1,3-cyclobutane-dione² (I) in neutral hydrogen peroxide (98%); the major product, formed in 85-90% yield after 11 days when the dione is treated with four equivalents of peroxide in acetonitrile solution, is the furandione³ shown below:



II

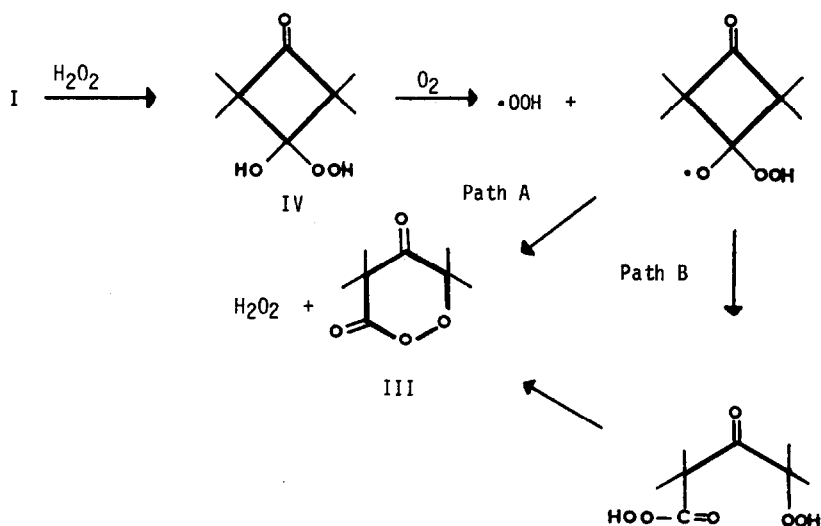
Compound II, m.p. 40-41⁰, exhibits the following spectral characteristics: $\nu_{C=O}$ (CCl₄) 1785, 1760 and 1750 cm^{-1} , nmr (CDCl₃) singlets of equal area at τ 8.45 and 8.62. The minor product of the reaction, formed in about 9% yield under the above conditions, is a compound whose properties are consistent with its formulation as a peroxyvalerolactone derivative:⁴



III

Lactone III³, m.p. 27⁰, exhibits the following spectral properties:
 $\nu_{C=O}(\text{CCl}_4)$ 1780 and 1735 cm^{-1} , nmr (CDCl_3) singlets of equal area at τ 8.49 and 8.42. Reduction of III with triphenylphosphine gives II and triphenylphosphine oxide.

Possible mechanisms for the formation of III are suggested as follows:



In either of these molecular oxygen would be required to initiate the dehydrogenation of the α -hydroxy hydroperoxide IV. In support of this, the yield of III is increased to 25% when oxygen is bubbled into the reaction mixture. Also, it is known that III is not a secondary product formed by further oxidation of II under the conditions described and that III is not formed at all when peroxytrifluoroacetic acid is substituted for hydrogen peroxide.

Although cyclization reactions of β -hydroperoxy acids or their esters have been used effectively to prepare the five-membered peroxy lactones,^{5,6,7} substantial difficulty has been encountered in attempts to prepare the six-membered ring systems. Thus, Cubbon and Hewlett have been unsuccessful in their attempt to prepare a peroxyvalerolactone derivative by cyclization of the gem-dihydroperoxide from levulinic acid⁸ and Adam and Szendrey have required strong acid media to cyclize the γ -hydroperoxy derivative of γ -methylvaleramide.⁴ For these reasons path A, in which ring expansion is concerted with or followed by abstraction of a second hydrogen atom, is presently preferred.

Irradiation of III, in degassed benzene solution, with a 450w Hanovia lamp effected its decomposition. Reaction was complete after nine hours and the only non-gaseous products which could be detected were acetone and dimethylketene; photolysis in benzene solution containing one equivalent of benzyl alcohol afforded benzyl isobutyrate in addition to acetone. This is to be contrasted with the photolysis of γ -methyl- γ -peroxyvalerolactone⁴ in which substantial yields of the oxetane (formed by loss of CO₂) could be detected. Thermolysis of III was complete after 5 minutes at 150⁰ and provides acetone and I; again, the dimethyl ketene first produced could be effectively trapped by performing the thermal decomposition in the presence of an equivalent of benzyl alcohol.

We are presently extending our studies to include other cyclic ketones in order to determine the mechanism and scope of the reaction.

References

1. a) E. J. Corey, Z. Arnold, and J. Hutton, Tetrahedron Lett., 307 (1970);
b) E. J. Corey and R. Noyori, ibid., 311 (1970).
2. Oxidation of this dione under Baeyer-Villiger conditions has been reported to yield II: See P. Y. Johnson and J. Yee, J. Org. Chem., 37, 1058 (1972).
3. Satisfactory analytical data have been obtained on this compound.
4. The first such compound has recently been reported: W. Adam and L. Szendrey Chem. Commun., 1299 (1971).
5. F. D. Greene, W. Adam, and G. A. Knudsen, J. Org. Chem., 31, 2087 (1966).
6. R. C. P. Cubbon and C. Hewlett, J. Chem. Soc., (C), 2983 (1968).
7. Dorothy H. Gibson and C. H. DePuy, Tetrahedron Lett., 2203 (1969).
8. R. C. P. Cubbon and C. Hewlett, J. Chem. Soc., (C), 2986 (1968).