

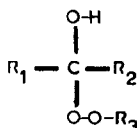
β -PEROXY- β -PROPIOLACTOLS:
CYCLIC ANALOGS OF THE BAEYER-VILLIGER INTERMEDIATE

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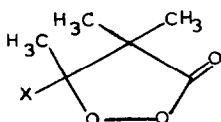
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The Baeyer-Villiger oxidation of simple ketones is a widely used synthetic tool in organic chemistry which involves the conversion of a ketone to an ester or a lactone by the action of a peroxy acid or hydrogen peroxide.¹ The key intermediate in these reactions is thought to be an α -hydroxy peroxide of the following general type:



Isolation of a compound of this type has proved to be difficult although an unstable adduct of related structure has been obtained from acetaldehyde and peroxyacetic acid.² We have prepared cyclic analogs of these intermediates by selective reductions of the β -hydroperoxy- β -peroxypropiolactones described below.

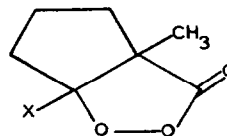
Reactions of ethyl- α,α -dimethylacetoacetate and 2-carbethoxy-2-methylcyclopentanone with 98% hydrogen peroxide containing catalytic amounts of sulfuric acid have provided the peroxypropiolactone derivatives Ia and IIa in 84% and 80% yield, respectively. This synthetic method parallels the one used by Cubbon and Hewlett³ to prepare β -hydroperoxy- β -methyl- β -peroxypropiolactone⁴ which was shown to involve the cyclization of an intermediate gem-dihydroperoxide. No attempt has been made to isolate the presumed intermediate gem-dihydroperoxides in the present work. Compound Ia is a colorless, crystalline solid⁵,



I

a, X = OOH

b, X = OH



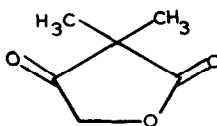
II

m.p. 82-83^o, which exhibits the following spectral characteristics: i.r. (CHCl₃) $\nu_{C=O}$ 1795 cm⁻¹, ν_{OH} 3500 and 3400 cm⁻¹; n.m.r. (CDCl₃) sharp singlets (3H each) at τ 8.43, 8.60 and 8.72 and a broad singlet at τ 0.81 (1H). Compound IIa⁵, m.p. 85-87^o, has the following spectral properties; i.r. (CHCl₃) $\nu_{C=O}$ 1790 cm⁻¹, ν_{OH} 3510 and 3400 cm⁻¹; n.m.r. (CDCl₃) singlet (3H) τ 8.60, multiplet (6H) τ 7.90 and a broad singlet (1H) at τ 0.80.

Careful reduction of Ia by slow addition of one equivalent of triphenylphosphine at 0^o afforded a molecular complex⁵ (1:1) between lactol Ib and triphenylphosphine oxide which has m.p. 92-99^o and whose i.r. spectrum (CHCl₃) indicates strong intramolecular hydrogen bonding⁶: ν_{OH} 3600 (weak) and 3160 (strong, broad) cm⁻¹. Compound Ib was obtained in > 95% yield by chromatography of the complex on silica gel; the lactol⁵, m.p. 82-83^o⁷, has the following spectral properties: i.r. (CHCl₃) $\nu_{C=O}$ 1795 cm⁻¹, ν_{OH} 3600 and 3490 cm⁻¹; n.m.r. (CDCl₃) sharp singlets (3H each) at τ 8.52, 8.70 and 8.75 and a broad singlet at τ 6.60 (1H). Similar reduction of IIa again provides a 1:1 molecular complex between triphenylphosphine oxide and the lactol, m.p. 79-80^o, whose i.r. spectrum also shows intramolecular hydrogen bonding: ν_{OH} 3600 (weak) and 3170 (strong, broad) cm⁻¹. The lactol was obtained in nearly quantitative yield by chromatography of the complex on silica gel; compound IIB⁵, m.p. 74-75^o, exhibits the following spectral properties: i.r. (CHCl₃) $\nu_{C=O}$ 1785 cm⁻¹, ν_{OH} 3580 and 3440 cm⁻¹; n.m.r. (CDCl₃) singlet (3H) τ 8.70, multiplet (6H) τ 8.00 and a broad singlet (1H) at τ 5.17. The reduction of either hydroperoxide may be effected equally well with triethylphosphite but, again, silica gel chromatography is necessary to obtain the pure lactol.

Thermal decomposition of Ib was effected in refluxing benzene solution during six hours; ring opening is attended by loss of CO₂, as with the β -peroxy- β -propiolactones studied by Adam and his co-workers⁸, and provides pivalic acid (characterized as the p-toluidide, m.p. 119-120^o, lit.⁹ 119-120^o) in about 90% yield. Irradiation of the lactol (in degassed benzene solution) for 15 hours with a 450 W lamp also yields pivalic acid as the major product (70% yield).¹⁰ Thermal and photochemical decompositions of IIB provide somewhat more complicated product mixtures than with Ib, however the major product (formed in about 80% yield) is an acid whose properties are in agreement with its formulation as 1-methylcyclobutanecarboxylic acid¹¹: i.r. (CHCl₃) $\nu_{C=O}$ 1700 cm⁻¹ and ν_{OH} 3100 cm⁻¹; n.m.r. (CDCl₃) singlet (3H) τ 8.55, multiplet (4H) τ 8.10, multiplet (2H) τ 7.50 and a further singlet (1H) at τ -0.87.

Compounds Ib and IIb are considerably more stable toward acid than the Baeyer-Villiger intermediates; upon standing at room temperature with one equivalent of trifluoroacetic acid Ib is completely converted to pivalic acid after 13 days, however, the conversion takes place at about the same rate without this acid. Reaction of Ib with conc. sulfuric acid at 0° occurs rapidly and provides a compound whose properties are in agreement with its formulation as a furandione^{12,5}:



III

The i.r. spectrum of III (CHCl_3) exhibits $\nu_{\text{C=O}}$ at 1800, 1770 and 1760 cm^{-1} and its n.m.r. spectrum (CDCl_3) exhibits singlets at τ 5.25 (1H) and 8.62 (3H). Compound IIb is more reactive toward trifluoroacetic acid than Ib; reaction in this case is complete after 3 1/2 days and yields a complex mixture of products which contains 1-methylcyclobutanecarboxylic acid as a minor component.

We are studying the reactions of these lactols in detail as well as trying to establish the phosphine reduction route as a general means of preparing them.

ACKNOWLEDGEMENT We thank the University of Louisville Arts and Sciences Research Committee for a research grant and American Standard for a Beckman IR-12 infrared spectrometer.

References

1. See J. B. Lee and B. C. Uff, *Quart Revs.*, **21**, 429 (1967) for a review of these reactions.
2. P. S. Starcher, B. Phillips, F. C. Frostick, Jr., *J. Org. Chem.*, **26**, 3568 (1961).
3. R. C. P. Cubbon and C. Hewlett, *J. Chem. Soc., C*, 2983 (1968).
4. This peroxy lactone was reported³ to be a shock sensitive oil; however, repeated crystallizations from CH_2Cl_2 -hexane yield the pure lactone, m.p. 46-48°.
5. Satisfactory microanalytical data have been obtained on a pure sample of this compound.
6. The i.r. spectra of weaker complexes from alcohols and triphenylphosphine oxide have been reported; see E. M. Arnett, L. Joris, E. Mitchell, T. S. S. R. Murty, T. M. Gorrie and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 2365 (1970).
7. The mixture m.p. of Ia and Ib is 65-70°.
8. W. Adam and Y. M. Cheng, *J. Amer. Chem. Soc.*, **91**, 2109 (1969).
9. Z. Rappoport, Ed., "Handbook of Tables for Organic Compound Identification", 3rd ed., The Chemical Rubber Co., Cleveland, Ohio, 1967, p. 193.

10. The photochemical decompositions of β -peroxy- β -propiolactones have been reported to yield epoxides as major products; see W. Adam and G. S. Aponte, J. Amer. Chem. Soc., **93**, 4300 (1971).
11. The acid has b.p. 42^o (0.2mm) and its p-toluidide⁵ has m.p. 108-109^o.
12. The related furandione which has four methyl groups is known and the spectral properties of III are similar to it; see Dorothy H. Gibson and J. T. Joseph, Tetrahedron Lett., 3483 (1972).