1,2,4-Trioxepans: Synthesis and Mass Spectral Behaviour

By WALDEMAR ADAM* and NELSON DURAN
(*Department of Chemistry, University of Puerto Rico, Rio Piedras, Puerto Rico* 00931)

Summary Acid-catalysed cyclization of γ-hydroperoxy-alcohols (**2**) into 1,2,4-trioxepans (**3**), a novel class of seven-membered ring peroxide heterocycles, and their mass spectral fragmentation is described.

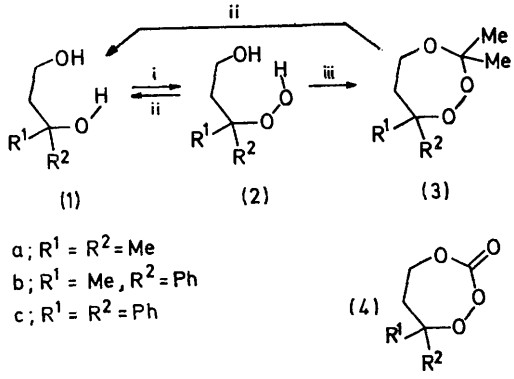
IN an investigation of oxygen diradicals, generated photolytically and pyrolytically from cyclic peroxides,[1] we have prepared 1,2,4-trioxepans (**3**) and attempted the preparation of 1,2,4-trioxepan-3-ones (**4**), both novel seven-membered ring peroxides. We considered using γ-hydroperoxy-alcohols (**2**) as precursors to (**3**) and (**4**), but no convenient preparations have been reported.[2]

The γ-hydroperoxy-alcohols (**2a**—**c**) were readily prepared, in 45—65% yield, by treatment of an ethereal solution of the respective diols (**1**) [prepared *via* reduction ($LiAlH_4$) of the corresponding Reformatsky esters] with 98% H_2O_2 at room temperature for 20—25 h in the presence of H_2SO_4 catalyst, as shown in the Scheme 1. Distillation or recrystallization afforded pure (98—100% by iodometric titration) (**2a**), b.p. 75—76° at 0·05 mmHg (n_D^{23} 1·4456); (**2b**), m.p. 44—45°; and (**2c**) m.p. 112—113°.†

Attempts to cyclize the γ-hydroperoxy-alcohols (**2**) to the cyclic peroxy-carbonates (**4**) with di-imidazolyl ketone or phosgene–pyridine even below −30° caused fragmentation

† Identified by i.r., n.m.r., and mass spectra, as well as catalytic reduction (Pd–C) to the respective diols (**1**).

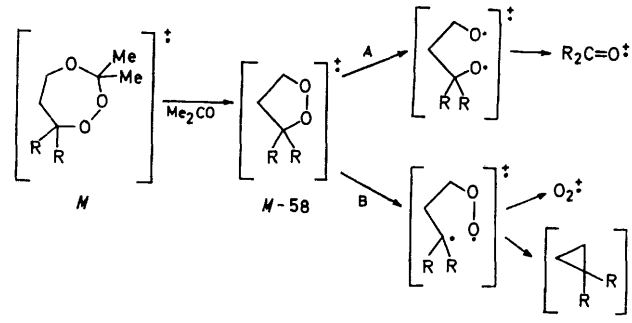
of (**2**), analogous to results with *vic*-hydroperoxy-alcohols.[3] However, treatment of (**2**) with acetone at room temperature, using toluene-*p*-sulphonic acid as catalyst, afforded the desired 1,2,4-trioxepans (**3a—c**) (50—60%) (see Scheme 1).



SCHEME 1. Reagents: i, H_2O_2–H^+; ii, H_2(Pd–C); iii, Me_2CO,-$MeC_6H_4SO_3H$.

Column chromatography on silica gel and molecular distillation, followed by g.l.c. or recrystallization gave pure (**3a**), b.p. 83—85° at 4·0 mmHg ($n_D^{21.5}$ 1·4272); (**3b**), b.p. 78—80° at 0·08 mmHg (n_D^{20} 1·5131); and (**3c**), m.p. 93—94°.†

As shown in Scheme 2 (only major charged fragments are shown), on electron impact the 1,2,4-trioxepans (**3**) expel acetone (confirmed by a metastable transition). As expected for 1,2-dioxolans,[4] and earlier demonstrated for 1,2,4-trioxolans (ozonides),[5] the resulting (M − 58) fragment suffers oxygen–oxygen cleavage (path A) to give the $R^1R^2C{=}O$ fragment, or alternatively suffers oxygen–carbon cleavage (path B) affording molecular oxygen and the cyclopropane fragments.



SCHEME 2.

We thank the National Science Foundation, the Petroleum Research Fund of the American Chemical Society, the Research Corporation, and the A. P. Sloan Foundation for financial support, the University of Puerto Rico for the purchase of the Hitachi-Perkin Elmer RMS-4 mass spectrometer, and Mr. J. Sanabia for the mass spectral analyses.

(*Received*, 10*th April* 1972; *Com.* 603.)

[1] W. Adam, O. L. Chapman, O. Rodriguez, R. Rucktäschel, and P. W. Wojtkowsky, *J. Amer. Chem. Soc.*, 1972, **94**, 1365; W. Adam and J. Sanabia, *J.C.S. Chem. Comm.*, 1972, 174; W. Adam and J. Baeza, *ibid.*, p. 103; W. Adam and J. C. Liu, *ibid.*, p. 73.
[2] N. A. Milas, U.S.P. 3,149,126 (1964) (*Chem. Abs.*, 1964, **61**, 15,977); Laporte Chemical Ltd., Fr. P. 1,343,360 (1963) (*Chem. Abs.*, 1963, **60**, 6750).
[3] W. Adam and A. Rios, *Chem. Comm.*, 1971, 822.
[4] W. Adam and N. Duran, to be published.
[5] J. Carles, Y. Rousseau, and S. Fliszar, *Canad. J. Chem.*, 1970, **48**, 2346.