

Perhydrolysis of Epoxides¹

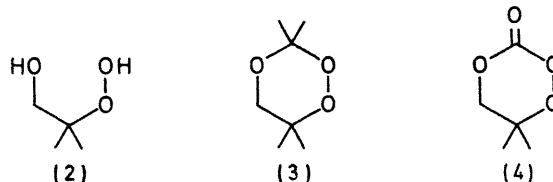
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Summary The reaction of epoxides with 98% hydrogen peroxide leads to the respective *vic*-hydroperoxy-alcohols.

In view of our interest in cyclic peroxides,² we required a convenient synthesis of *vic*-hydroperoxy-alcohols (**2**) as synthons in the preparation of the novel 1,2,4-trioxans (**3**) and cyclic peroxy-carbonates (**4**). A recent communication,³ which describes the isolation of 2-hydroperoxy-2-methylpropan-1-ol (**2a**) in the molybdenyl acetylacetonate-catalysed reaction of isobutylene oxide (**1a**) with anhydrous hydrogen peroxide, prompts us to communicate our preliminary results on the uncatalysed perhydrolysis of epoxides (**1**).

When a solution of isobutylene oxide (**1a**) and 98%



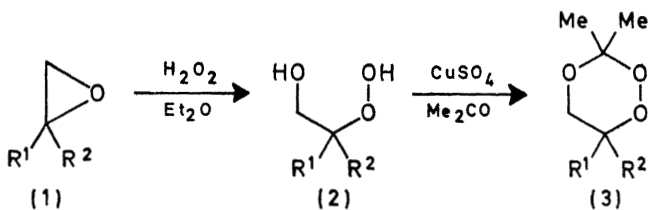
hydrogen peroxide in ether was stirred at room temperature for 14 days, distillation of the reaction mixture at reduced pressure gave (**2a**) in 70% yield, b.p. 72–73°/0.07 mm, n_D^{20} 1.4425, 84% pure by iodometric titration. All efforts at effecting further purification by distillation or column chromatography failed, since it proved difficult to separate

the corresponding diol impurity from the hydroperoxy-alcohol. The structural assignment rests on the facts that catalytic hydrogenation over Pd/C gave the expected diol in 95% yield, and that the i.r. and n.m.r. spectra are identical with those described by Perrotti and his co-workers.³ Treatment of (2a) with acetone in the presence of anhydrous cupric sulphate gave a 50% yield of 3,3,6,6-tetramethyl-1,2,4-trioxan (3a), b.p. 60–61°/23 mm, n_D^{20} 1.4183. Trioxan (3a) on catalytic hydrogenation over Pd/C gave the expected diol (85% yield).

Similarly, perhydrolysis of α -methylstyrene oxide (1b) gave the hydroperoxy-alcohol (2b) in 80% yield, m.p. 65–71°, 97% pure by iodometric titration, and 1,1-diphenylethylene oxide (1c) gave (2c) in 92% yield, m.p. 123–124°, 99% pure by iodometric titration. Furthermore, the hydroperoxy-alcohols (2b) and (2c) could be cyclized to their trioxan derivatives (3b) and (3c) in 54 and 51% yields, respectively. The n.m.r. and i.r. spectra are consistent with the structures suggested, and catalytic reduction of the hydroperoxy-alcohols (2b) and (2c) and the trioxans (3b) and (3c) gave the expected diols in high yields.

Attempts to cyclize the *vic*-hydroperoxy-alcohols (2) into the cyclic peroxy-carbonates (4) with phosgene in pyridine or di-imidazolyl ketone has so far resulted in ketonic decomposition products, over a wide range of conditions. Even at

temperatures as low as -40° , the hydroperoxy-alcohol (2c) gave benzophenone almost quantitatively. These same ketonic decomposition products are also formed when the hydroperoxy-alcohols (2) are treated with strong acid catalysts.



- a; $R^1 = R^2 = \text{Me}$
 b; $R^1 = \text{Me}, R^2 = \text{Ph}$
 c; $R^1 = R^2 = \text{Ph}$

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² W. Adam and R. Rucktäschel, *J. Amer. Chem. Soc.*, 1971, **93**, 557; W. Adam, Y. M. Cheng, C. Wilkerson, and W. A. Zaidi, *ibid.*, 1969, **91**, 2111; W. Adam, R. J. Ramirez, and S. C. Tsai, *ibid.*, p. 1254.

³ A. M. Mattucci, E. Perrotti, and A. Santambrogio, *Chem. Comm.*, 1970, 1198.