

Stereoisomeric 1,2,4,6,7,9-Hexaoxecan Derivatives from Dimerisation of a 1,2,4-Trioxolan; Stereospecific Interconversion

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Carbon disulphide and other acceptors catalyse the dimerisation of the endoperoxide formed from photo-oxygenation of 1,3-diphenylisobenzofuran to mixtures of four stereoisomeric diperoxides; pairs of these dimers are stereospecifically interconvertible on gentle heating.

Despite much work on peroxides^{1a} and ozonides (1,2,4-trioxolans),² there have been only a few reports on their dimerisation. Dimers previously obtained include an unstable 1,2,5,6-tetraoxocan,³ derivatives of 1,2,4,5-tetraoxan and 1,2,4,5,7-pentaoxocan^{4a,4b} (and *cis-trans* isomerisation of a 1,2,4,5-tetraoxan^{4c}), a peroxide dimer,⁵ and a tricyclic diperoxide.⁶

The ozonide-type endoperoxide (2) of (1), prepared in diethyl ether solution, shows unusual reactivity.⁷ We now report another novel reaction of (2), *viz.* its carbon disulphide-induced dimerisation. At high concentrations the reaction is exothermic and even explosive at room temperature. In early attempts⁸ to isolate (2), explosions occurred on warming to *ca.* 18 °C the crystalline peroxide resulting from evaporation

of its carbon disulphide solution after low temperature photo-oxidation of (1) in this solvent.

A transient yellow colour appears rapidly. Moderate dilution of CS₂ with neutral solvents (toluene, cumene), at any time, does not affect the dimerisation. In contrast, early dilution (before the appearance of the colour) with methanol and weakly basic solvents [tetrahydrofuran (THF) and, less efficiently, diethyl ether] quenches the dimerisation, methanol giving the addition product (methoxy-hydroperoxide).⁷ Methanol and THF, added later, are ineffective.

We attribute the catalytic effect of CS₂ to its dipolar character.⁹ Other acceptors, such as tetracyanoethylene and 4-phenyl-1,2,4-triazoline-3,5-dione, also catalyse, to a lesser extent, the dimerisation of (2). Lewis acids, such as BF₃ at

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References

- 1 (a) O. L. Mageli and C. S. Sheppard, in 'Organic Peroxides,' ed. D. Swern, Wiley, New York, 1970, vol. I, p. 29; (b) R. Hiatt, *ibid.*, 1971, vol. II, p. 105; (c) G. Sosnovsky and D. J. Rawlinson, *ibid.*, pp. 161 and 187.
 - 2 P. S. Bailey, 'Ozonation in Organic Chemistry,' Academic Press, New York, 1978, vol. 1, p. 33.
 - 3 E. H. White, N. Suzuki, and W. H. Hendrickson, *Chem. Lett.*, 1979, 1491 (water-catalysed dimerisation of a 1,2-dioxetan).
 - 4 (a) M. Miura and M. Nojima, *J. Chem. Soc., Chem. Commun.*, 1979, 467; *J. Am. Chem. Soc.*, 1980, **102**, 288; (b) M. Miura, M. Nojima, S. Kusabayashi, and S. Nagase, *ibid.*, 1981, **103**, 1789 (reaction of ozonides with $SbCl_5$ or $ClSO_3H$); (c) M. Miura, M. Nojima, and S. Kusabayashi, *J. Chem. Soc., Perkin Trans. 1*, 1980, 1950.
 - 5 C. S. Foote, M. T. Wuesthoff, S. Wexler, I. G. Burstain, R. Denny, G. O. Schenck, and K.-H. Schuite-Elte, *Tetrahedron*, 1967, **23**, 2583 [spontaneous dimerisation of a furan endoperoxide to a dimer, the structure of which is probably similar to (7)].
 - 6 J. Banerji, N. Dennis, A. R. Katritzky, R. L. Harlow, and S. H. Simonsen, *J. Chem. Res.*, 1977, (S) 38; (M) 0517 (photo-oxidation of a pyridinium-3-olate).
 - 7 G. Rio and M.-J. Scholl, *J. Chem. Soc., Chem. Commun.*, 1975, 474.
 - 8 Ch. Dufraisse and S. Ecary, *C. R. Acad. Sci.*, 1946, **223**, 735; S. Ecary, *Ann. Chim. (Paris)*, 1948, **3**, 445.
 - 9 J. F. Willems, *Fortschr. Chem. Forsch.*, 1963, **4**, 554.
 - 10 A. Le Berre and R. Ratsimbazafy, *Bull. Soc. Chim. Fr.*, 1963, 229; J. A. Howard and G. D. Mendenhall, *Can. J. Chem.*, 1975, **53**, 2199.
 - 11 Complexes dioxetan-water (ref. 3) and metalloporphyrins (S. P. Schmidt and G. B. Schuster, *J. Am. Chem. Soc.*, 1980, **102**, 7100) have been characterised.
 - 12 The related 1,3,3-triphenylisobenzofurylium ion is yellow (S. V. Yakovlev and L. A. Pavlova, *Zh. Org. Chim.*, 1968, **3**, 852; J. Rigaudy and C. Brelière, *Bull. Soc. Chim. Fr.*, 1972, 1390).
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