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 photooxygenation 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 CS_2 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 CS_2 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 BF_3 at



moderate concentration (ca. 0.02-0.2 M) in diethyl ether solution, ZnCl₂, and FeCl₃, act similarly. At lower concentrations (ca. 2-4 mM), BF₃ gives a polymeric peroxide† similar to that obtained by autoxidation of (1).¹⁰

From the reaction of (2) with the above catalysts, four stereoisomeric dimers, of the five possible ones, may be isolated in pure form: two slightly soluble, (7a), m.p. 320-324 °C (decomp.), and (7b), m.p. 290-295 °C (decomp.), one fairly soluble, (7c), m.p. 300-305 °C (decomp.), and one barely soluble, (7d), m.p. 315-320 °C (decomp.). The relative yields depend on catalyst, concentration of (2), and temperature. Representative results are: (2) (0.65 M), CS₂, -12 °C, 1 h give (7a) 22, (7b) 7, and (7d) 3.5%; (2) $(3.25 \times 10^{-2} \text{ M})$, CS₂, -12 °C, 2 h give (7a) 24, (7b) 14, and (7d) 3.8%; (2) (0.65 м), 4-phenyl-1,2,4-triazoline-3,5-dione (sat.), chlorobenzene, 0 °C, 45 min give (7a) 6, (7b) 3, (7c) 5, and (7d) 5%. Other products isolated were the diketone (8),⁷ the ketoester (11),⁷ the acyloxyketone (10)⁷ and the peroxy-dihydroperoxide (6). The most soluble dimer, (7c), is conveniently prepared [47%; (7d)]49%] by oxidative lead(IV) acetate cyclisation^{1b,1c} of the peroxy-dihydroperoxide (6). The latter is obtained in only one of the six possible isomeric forms, m.p. 250 °C (decomp.) (50%), on addition of the dihydroperoxide (5) to the peroxide (2). The dihydroperoxide (5) (mixture of isomers) results (70%) from similar addition of H_2O_2 to the peroxide (2). It is also obtained from (1) by addition of bromine in the presence of pyridine, followed by treatment with hydrogen peroxide-urea.

The structure (7) for all the dimers was deduced from their analytical data, m.w. (osmometry) (7a) 540, (7b) 490, and (7c) 560, i.r. (absence of OH and CO absorption), Raman [ν (OO): (7a) 845, (7b) 825, (7c) 861, and (7d) 826 cm⁻¹], and u.v. spectra (benzene absorption).‡ In the u.v. spectra, the greater intensity of (7b) and (7d) (ϵ ca. 3000 dm³ mol⁻¹ cm⁻¹ at 260 nm) than that of (7a) and (7c) (ϵ ca. 2000) is ascribed to a more severe ring strain.§ Inspection of Dreiding models shows that the *trans-syn-trans* and *trans-anti-trans* isomers are very strained. We suggest that the catalytic role of the acceptors such as CS_2 is the formation from (2) of the zwitterions (3) and (4).¹¹ The transient yellow colour is possibly that of (4).¹²

Reduction (HI-AcOH) of the dimers to the diketone (8) [and some ketoester (11)] and Baeyer-Villiger rearrangement (H₂SO₄ 18 M) to (11) [and some (8)] are in accord with the structure (7).7 Decomposition of the diperoxides (7) on prolonged heating (chlorobenzene, 132 °C) gives the diketone (8), and probably oxygen. On shorter heating, or at lower temperatures, interconversion of the dimers occurs stereospecifically in pairs: $(7a) \rightleftharpoons (7b)$, $(7c) \rightleftharpoons (7d)$. Representative conditions are: toluene or nitroethane (30 min) at 110 °C for the former pair [(7a) predominant]; for the latter pair various solvents at room temperature from (7c), chlorobenzene at 132 °C (30 min) from (7d) (predominant, owing to its very low solubility). Interconversion $(7c) \Rightarrow (7d)$ is faster in a polar solvent (nitroethane) than in a weakly polar one (benzene). The stereospecificity of the interconversions is in accord with a mechanism involving ionisation to the pair of zwitterions (12), related to (3), and recombination with inversion of configuration of two carbon atoms at once. This would effect the conversions cis-syn-cis \Rightarrow trans-anti-trans and cis-anti $cis \rightleftharpoons trans-syn-trans$. These four isomers all possess a symmetry elements and we believe that these are the four isomers we have. From the molecular models, u.v. spectra, and stereospecificity of interconversion, we tentatively suggest that (7b) and (7d) are the *tst* or *tat* isomers, (7a) and (7c) being *csc* or cac.

We thank Mrs L. Lacombe (Collège de France), Mrs M.-P. Simonnin, Mrs M.-J. Pouet, and Mrs A. Cordaville (E.N.S.C., Paris) for n.m.r. spectra, Mrs J. Zarembowitch, Mrs Voyron, and Miss H. Le Pesant (E.N.S.C., Paris) for vibrational spectra, Dr. P. Hémery (Collège de France) for osmometric m.w.

[†] M.p. ca. 200 °C (decomp.), m.w. ca. 2800—3700, far more soluble than the dimers (7).

 $[\]ddagger^{13}$ C N.m.r. spectrum of the most soluble, (7c): eight peaks (symmetrical configuration).

[§] A strained phthalan derivative such as (2) has a greater absorption (ϵca . 1800 dm³ mol⁻¹ cm⁻¹) than that of less strained ones, (9; R = H, OMe isomers or R-R = O[CH₂]_nO, n = 2,3) ϵca . 700—1200 dm³ mol cm⁻¹ and (6) ϵca . 2300 dm³ mol⁻¹ cm⁻¹, [two phthalan units, like (7)]. Compounds (9; R = OMe isomers) m.p. 105—110 °C and 115—120 °C, (9; R-R = O[CH₂]₂O) m.p. 98—100 °C, then 110 °C (dimorphism), (9; R-R = O[CH₂]₂O) m.p. 128 °C result from reaction of MeOH or HO[CH₂]_nOH with the addition product (1)-bromine-pyridine.

determinations, the Centre de recherches Roussel-UCLAF for microanalyses, and a referee for helpful comments.

Received, 25th August 1981; Com. 1031

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