

1,1-Dihydroperoxycyclododecane

T. LEDAAL and T. SOLBJÖR

Universitetets Kjemiske Institutt, Blindern, Oslo 3, Norway

Only a few geminal dihydroperoxy compounds have so far been prepared. Among these are 9,9-dihydroperoxyfluorene,¹ 1,1,6,6-tetrahydroperoxycyclododecane,² and different sterols with dihydroperoxy-groups in positions 3, 17, or 20.^{3,4}

Strong indications for the existence of geminal dihydroperoxides have further been obtained by chromatographic means^{5,6} and by the isolation of diperbenzoates.¹

One of the present authors (T.L.) reports elsewhere on a simple method for preparation of ketone peroxides.⁷ By this method the following ketone peroxides, among others, have been isolated: the dimeric peroxides of cycloheptanone, cyclooctanone, cyclododecanone, and cyclopentadecanone. The former two are the first well-defined peroxides obtained from cycloheptanone and cyclooctanone, respectively. The structure of these have been determined by Groth^{8,9} by X-ray crystallography.

In this paper we report on 1,1-dihydroperoxycyclododecane, the preparation of which was achieved by treating cyclododecanone with 34 % hydrogen peroxide. The new compound has been obtained in three different ways, 1) by reacting the ketone with excess hydrogen peroxide in propionic acid, 2) from nearly stoichiometric amounts of the reagents in acetonitrile, and 3) by using formic acid instead of acetonitrile as a solvent. The yields were not very different for the three procedures, but the reaction time (at 20°C) varied from a few days in the first to a couple of minutes in the last case.

The dihydroperoxide is a well defined compound, crystallizing in colourless prisms, which melt fairly sharply at 140°C. It can be stored for months at or below 0°C, and only minor decomposition can be observed after storage for several weeks at room temperature. The substance analyses correctly for the elements and for active oxygen, and gives the calculated molecular weight. Upon treatment with benzoyl chloride small amounts of the diperbenzoate could be isolated. The hy-

droperoxide readily liberates iodine from neutral solutions of iodide in acetonitrile with simultaneous evolution of oxygen. With titanil ions in acidic solutions a yellow colour develops, the intensity of which increases with time. In this reaction the hydroperoxide gives nearly quantitatively hydrogen peroxide and cyclododecanone in the mole ratio 2/1.

The infrared spectrum shows two different peaks within the hydroperoxy O—H stretching region at 2.93 μ and 3.00 μ , and C—O and O—O vibrations at 9.43, 10.50, and 11.83 μ .

The NMR spectrum shows peaks at the τ -values —0.05, 8.25, and 8.73 with relative intensities 2:8:14.

The above-mentioned facts may indicate a preferred conformation for 1,1-dihydroperoxycyclododecane where the oxygen atoms of a hydroperoxy group comes very near four hydrogen atoms of the ring as seen from inspection of Stuart molecular models. These four ring hydrogen atoms show an NMR absorption in the same region as the four α -hydrogen atoms, giving the observed integrated values of totally eight ring hydrogens at the somewhat lower and fourteen at the higher τ -value.

Experimental. Chemicals used were *p.a.* Merck if not otherwise stated.

Preparation of the hydroperoxide. Expt. 1. 1.82 g cyclododecanone (Aldrich) was dissolved in 25 ml propionic acid. Two drops of perchloric acid dihydrate and 5 ml 34 % hydrogen peroxide were added with stirring. The mixture was left in an open jar in a fume hood for 3 days at *ca.* 20°C. Colourless crystals which had separated were filtered off, washed with cold water and dried *in vacuo* (0.90 g, m.p. 134°C). After recrystallizing twice from petroleum ether (b.p. 60–70°C) and washing with cold pentane, colourless prisms, melting sharply at 140°C, were obtained.

Expt. 2. As for expt. 1 but with acetonitrile as solvent instead of propionic acid, and using 2 ml of hydrogen peroxide. 2.0 g of colourless, crude product melting at *ca.* 78°C resulted. Washing with pentane, recrystallization from benzene and a final washing with pentane gave 1.10 g fine crystals, m.p. 134°C.

Expt. 3. To 1.82 g cyclododecanone in 10 ml formic acid was added 2.0 ml of 34 % hydrogen peroxide dropwise with stirring. After continued stirring for 2 min the solid was filtered off, washed with cold sodium bicarbonate solution, then with ice-water and dried *in vacuo* (2.10 g, m.p. 78°C). Further treatment

as under expt. 2 yielded 1.10 g crystals, m.p. 134°C.

Mixed m.p. of crystals from the three experiments showed no depression, and the spectra (data given in text above) were identical. (Found: C 62.08; H 10.43. Calc. for $C_{12}H_{24}O_4$:C 62.05; H 10.52). Molecular weight was determined with a vapour pressure osmometer. Found: 233, calc. 236. Total active oxygen: Found 13.4 %, calc. 13.5 %.

(Samples of ca. 10 mg were treated with a 10 % solution of sodium iodide in acetonitrile acidified with perchloric acid dihydrate. The mixture was left in a completely filled stoppered flask stored in the dark at ca. 20°C for 15 min and titrated with 0.01 N thiosulphate solution. A blank was run under the same conditions.)

Determination of hydrogen peroxide and ketone after treatment with titanil reagent: The hydroperoxide was left for 24 h with excess titanil reagent. The hydrogen peroxide was determined iodometrically as described elsewhere,¹⁰ while the ketone was filtered off, dried and weighed.

IR spectra were taken with a Beckman IR5A spectrophotometer. NMR: A Varian Associate Spectrometer operating at 60 Mc/sec was used with TMS as an internal standard.

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On the Crystal Structure of Sn_4P_3

OLLE OLOFSSON

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

The occurrence of several intermediate phases in the tin-phosphorus system has been reported in earlier literature. Depending on the difficulties in determining the phase conditions, however, the data have often been contradictory. The three most recent investigations will be mentioned here. In 1909 Jolibois¹ found a compound Sn_4P_3 by means of electrolytical isolation. A compound SnP_3 was also stated to exist. A more systematic investigation using physico-chemical methods was made by Vivian in 1920.² Using thermal, microscopic, and residue analytical methods the three intermediate phases Sn_4P_3 , Sn_3P_4 , and SnP_3 were found. Later (1957) Katz *et al.*³ published X-ray powder data for a phase which they found to be of the composition SnP . This seems to be the only X-ray investigation that has been made of the tin-phosphorus system. All the phases mentioned are in need of further characterization.

An investigation has been started at this institute in order to obtain more information on the tin-phosphorus system. In this paper X-ray powder data will be given for a phase with the ideal crystallographic composition Sn_4P_3 , together with preliminary results from a single-crystal structure determination.

The starting materials for the preparations were tin powder (KEBO, purum) or tin rods (Johnson, Matthey & Co., Ltd, spectrographically standardised, containing in ppm: Pb 5, Bi 2, Ca and Cu both < 1) and red phosphorus (purity higher than 99 %). The syntheses were performed by heating weighed amounts in evacuated and sealed silica tubes at temperatures between 400°C and 545°C. The reaction products were examined by X-ray powder methods in Guinier-Hägg-type focussing cameras using $CuK\alpha_1$ or $CrK\alpha_1$ radiation. Silicon ($a = 5.43054 \text{ \AA}$) was used as an internal calibration standard.

Preliminary results of this phase analysis confirm the existence of a phase near the composition Sn_4P_3 , and indicate the existence of the phase reported to be SnP .³ However, there are indications that this phase is a low-temperature phase formed