



Fig. 1. Proposed pathway in the biosynthesis of cycloalliin from cysteine.

*trans*-configuration. Experimental evidence is still lacking for some of the intermediate steps, but work is in progress to elucidate this reaction sequence further.

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## A Simple Laboratory Method for the Preparation of (Dimeric) Ketone Peroxides

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Peroxides from the reaction between simple cyclic ketones and hydrogen peroxide have been isolated and studied by many workers, among others by Milas,<sup>1</sup> Criegee,<sup>2</sup> Cooper,<sup>3</sup> Hawkins,<sup>4</sup> Kharasch,<sup>5</sup> Stoll and Scherrer,<sup>6</sup> and Halbig.<sup>7</sup> In the case of cycloheptanone and cyclooctanone the reaction has been reported to result in mixtures, from which no single well-defined peroxide could be isolated.<sup>8</sup>

The present author has prepared different known and some new ketone peroxides by a simple method which will be described below. The method consists of treating the ketones with 34 % hydrogen peroxide under conditions which allow a facile removal of the water from the aqueous hydrogen peroxide as well as that formed during the reaction. Reaction mixtures are spread in a thin layer on a glass or other suitable surface, and subjected to a stream of dry air. Most simply the layer is left over night in a fume hood. By spraying the reaction mixture over a

semiporous surface of baked clay which has been slightly moistened over boiling water, the reaction time can in some cases be reduced to a few minutes. The crystalline peroxides formed are washed with small quantities of ice-water, dried *in vacuo* and recrystallized from petroleum ether at temperatures well below the melting points for the crude products.

A general method of transforming the different hydroperoxides first formed into dimeric peroxides or 1,2,4,5-tetraoxacyclohexanes\* is as follows: The peroxides are dissolved (or if slightly soluble, dispersed) in the minimum quantity of a cold carboxylic acid, preferably propionic acid. A few drops of perchloric acid dihydrate are added and the solution is kept at 0°C for half an hour. The crystals that in most cases have been separated or will separate by scratching with a glass rod, are filtered off, washed with cold water and dried. To the filtrate is slowly added three times its volume of ice-water. After an hour with occasional stirring the solid is filtered off, washed with cold water, dried and recrystallized from acetonitrile. Yields varying from 20 to 75% of dimeric peroxides are obtained by this simple acidolysis procedure. As a by-product a peracid is formed in varying amounts. Dimeric peroxides from cyclohexanone, cycloheptanone, cyclooctanone, cyclododecanone, and cyclopentadecanone were prepared by this method.

By X-ray crystallography Groth has recently solved the structure of the dimeric peroxides of cyclohexanone,<sup>9</sup> cycloheptanone,<sup>10</sup> and cyclooctanone.<sup>11</sup>

*Experimental.* Reaction mixtures consisting of 10 mmoles each of cyclic ketone and 34% aqueous hydrogen peroxide, 2 drops of perchloric acid dihydrate and 10 ml acetonitrile were left open to atmosphere in a fume hood

\* In the case of cyclopentanone only the trimeric peroxide is formed, and for cyclododecanone and cyclopentadecanone a dimeric dihydroperoxide is formed in about twice the amount of the dimeric peroxide.

for 24 h at ca. 20°C. The crude products of hydroperoxides which resulted, were washed, dried and transformed to dimeric peroxide in the above-mentioned way with the following results:

*Dimeric cyclohexanone peroxide.* Yield ca. 60%, m.p. 132°C. (Found: C 63.24; H 8.81. Calc. C 63.60; H 8.83. Found active oxygen 13.9%, calc. 14.0).

*Dimeric cycloheptanone peroxide.* Yield 75%, m.p. 103°C. (Found: C 65.56; H 9.42. Calc. C 65.60; H 9.40. Found active oxygen 12.4%, calc. 12.5).

*Dimeric cyclooctanone peroxide.* Yield ca. 20%, m.p. 98°C. (Found: C 67.04; H 9.82. Calc. C 67.60; H 9.85. Found active oxygen 11.1%, calc. 11.2).

*Dimeric cyclododecanone peroxide.* Yield ca. 25%, m.p. 201°C. (Found: C 72.79; H 11.02. Calc. C 72.70; H 11.10. Found active oxygen 8.0%, calc. 8.1).

*Dimeric cyclopentadecanone peroxide.* Yield ca. 30%, m.p. 173°C. (Found: C 75.11; H 11.69. Calc. C 74.97; H 11.70. Found active oxygen 6.5%, calc. 6.7).

Molecular weights were checked with a vapour pressure osmometer, structures by IR and NMR spectra.

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