



Figure 2. Attack by singlet oxygen on the *re-re* face of **2** in the $(P)\text{-}(+)\text{-}1$ clathrate generates hydroperoxide **4** of *R* configuration (a). Development of the same nonbonded interactions requires singlet oxygen to attack the *si-si* face of the $(M)\text{-}(-)\text{-}1$ clathrate to give **4-S** (b).

a host to guest ratio of 2:1. The orientation of the guest **2** within the cavity was ascertained from a Fourier difference synthesis of the clathrate **1/2**. The enol ether **2** adopts a disordered, static arrangement consistent with the local 2-fold symmetry. The crystallographic 2-fold axis bisects the central olefinic bond and passes through the oxygen atom (Figure 1). Three *s-cis* conformations are observed, each of which has torsion angles ($C=C-O-C$ (θ)) of 0° , $+60^\circ$, and -60° , respectively. The planar achiral conformation is the least populated, while the two gauche, and therefore chiral, conformations ($\pm 60^\circ$) are equally populated.

In a typical experiment, crystals of clathrate $(P)\text{-}(+)\text{-}1/2$ (16.18 mg) were mixed with ion exchange resin (IRA 401) to which rose bengal was fixed.¹⁰ The mixture of particles was tumbled in a stream of oxygen and irradiated for 160 h with two Sylvania FFX 500-W lamps equipped with a cutoff filter at 418 nm. The resulting mixture was dissolved in hexadeuteriobenzene (1 mL), which destroyed the clathrate with concomitant racemization of the host molecule. The resulting solution was examined by NMR

(8) Gerdil, R.; Allemand, J. *Tetrahedron Lett.* **1979**, *37*, 3499–3502. Allemand, J.; Gerdil, R. *Acta Crystallogr., Sect. B* **1982**, *B38*, 2312–2315.
 (9) X-ray data were collected by using a Philips PW 1100 four-circle automatic diffractometer.

(10) The clathrate sample was mixed with 250 mg of sensitizer, which consisted of 0.385 g of RB/g of resin. The two sets of particles were agitated and irradiated in a cooled (15°C) cuvette.

spectroscopy,¹¹ whence a yield of 30% was determined for the hydroperoxide **4**. The same solution revealed by polarimetry¹² a residual optical activity of $+0.060^\circ$. This experimental value corresponds to a specific rotation¹³ ($[\alpha]_{546}^{20}$) of $+120 \pm 20^\circ$ for **4**. In another experiment the clathrate of opposite configuration was used, namely, $(M)\text{-}(-)\text{-}1/2$ (12.47 mg). The same procedure gave the hydroperoxide **4** in 27% yield. Polarimetry showed a residual rotation of -0.051° , corresponding to a specific rotation of $-146 \pm 20^\circ$. Although the optical purity of the hydroperoxides (**4**) obtained in these two experiments is unknown, the similarity of amplitude and complementarity of sign of the rotations are significant.

We believe that these results demonstrate the first example of the heterogeneous transfer of chirality from the dissymmetric cavity of a host to its prochiral guest while undergoing reaction. How this transfer occurs is problematic. Since neither of the chiral, gauche conformations of **2** is preferred in the ground state, it may be inferred that stereodifferentiation occurs during the creation of the pyramidal center at the vinyl terminus of **2** in the chiral environment. In other words, singlet oxygen permeates the cavity of the host and reacts with **2** by two diastereotopic transition states. If it is assumed that one of these states favors attack by singlet oxygen on the *re-re* face of **2** in the $(P)\text{-}(+)\text{-}1/2$ clathrate, then **4-R** will be formed (Figure 2). In order that the same nonbonded interactions are developed in $(M)\text{-}(-)\text{-}1/2$, attack by singlet oxygen is required on the *si-si* face, thereby giving **4-S**. Once the chiral host is removed, the product remaining appears to be the result of an enantioselective reaction.

Acknowledgment. We are indebted to the Swiss National Science Foundation for support of this work (Grants No. 2.035-0.83 and 2.036-0.83). G.B. is grateful to the Harbor Branch Institution, Fort Pierce, FL, for the provision of a stipend.

(11) In the solid phase the only product formed was the hydroperoxide **4**, the yield of which was estimated from the relative intensities of the proton NMR signals of the methoxy groups of **4** and **2**.

(12) Optical rotations were determined on a Perkin-Elmer Model 241 polarimeter. The maximum amount (in grams) of hydroperoxide **4** produced by *w* grams of clathrate is given by the ratio $wM(4)/[M(2) + 2M(1)]$, which accounts for the host-guest stoichiometry, where *M* is the molecular weight. After correction of the observed rotation for the reaction yield, $[\alpha]$ is calculated¹³ with the concentration of **4** expressed in g/100 mL.

(13) Correctly speaking, specific rotation characterizes a pure enantiomer, which is probably not the case. Nevertheless, the value obtained represents a lower limit that is sufficiently large to indicate a substantial, but undetermined, enantiomeric excess.

Additions and Corrections

Structurally Ordered Bimetallic One-Dimensional catena- μ -Dithiooxalato Compounds: Synthesis, Crystal and Molecular Structures, and Magnetic Properties of $AMn(S_2C_2O_2)_2(H_2O) \cdot 4.5H_2O$ (*A* = Cu, Ni, Pd, Pt) [*J. Am. Chem. Soc.* **1984, *106*, 3727–3737]. ALAIN GLEIZES and MICHEL VERDAGUER***

Page 3729: In Table III, the positional and thermal parameters of the copper atom Cu in $CuMn(S_2C_2O_2)_2(H_2O)_3 \cdot 4.5H_2O$ are missing. They are as follows: $x = 0.28723$ (21); $y = 0.25181$ (17); $z = 0.2070$ (4).