μ-{C(CF$_3$)=C(CF$_3$)C(CF$_3$)=C(CF$_3$)}PdCH(SiMe$_3$)C$_6$H$_4$N-Me$_2$] and the stabilization of the dinuclear structure is under investigation.

A mechanism for the formation of these dinuclear Pd compounds must account for both the exclusive formation of the unsymmetric coupling product **4** and the fact that the Pd centers bear different ring systems, whereas these are present in a 1/1 ratio in the mononuclear Pd starting product. A possible route involves intramolecular oxidative coupling of the cyclometalated rings induced by coordination of the butynes with subsequent formation of a palladocyclopentadiene. Reaction of this intermediate with unreacted **2** may then form a dinuclear species which finally forms **3** via an intramolecular exchange of the organo groups (bridging C groups; Scheme IIa).[12]

However, a likely alternative, in view of our earlier findings concerning the insertion of butynes in Pd–C bonds, comprises prior formation of a dinuclear Pd intermediate containing both a N⌒C bridging dmba or 8-mq and a Me$_2$NC$_6$H$_4$CH(SiMe$_3$) group as well as the coordinated butyne. Subsequent intramolecular C'–C coupling reactions of both the bridging C⌒N ligand and the two butynes then forms **3** (Scheme IIb).

Our present studies are directed to find further support for the mechanistic as well as the bonding aspects of these novel compounds.

Acknowledgment. We thank the CNRS for partial support and Dr. A. L. Spek for helpful discussion.

Supplementary Material Available: NMR data for **2a,b**, **3a,b**, and **4b** and a molecular structure diagram (2 pages). Ordering information is given on any current masthead page.

(12) Van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K. *J. Organomet. Chem.* **1981**, *222*, 155.

(13) Examples of alkyne oligomerization on dimetallic centers have already been described in the literature,[14] but to our knowledge this is the first such case where this occurs between nonequivalent metal atoms.

(14) Dickson, R. S.; Fraser, P. J.; Gatehouse, B. M. *J. Chem. Soc., Dalton Trans.* **1972**, 2278. Green, M.; Norman, N. C.; Orpen, A. G. *J. Am. Chem. Soc.* **1981**, *103*, 1269.

Heterogeneous Chirality Transfer on Photooxygenation

Raymond Gerdil, Giacomo Barchietto, and
Charles W. Jefford*

*Department of Organic Chemistry
University of Geneva, 1211 Geneva 4, Switzerland*

Received August 8, 1983

Asymmetry is usually induced in an organic reaction by employing chiral reagents and catalysts.[1] Under special circumstances, the chirality associated with polarized light[2] and crystal lattices[3] has also been used. We now report a novel case of induction where the dissymetric cavities within tri-*o*-thymotide (**1**) crystals[4] impart asymmetry to the reaction of an enclathrated substance.
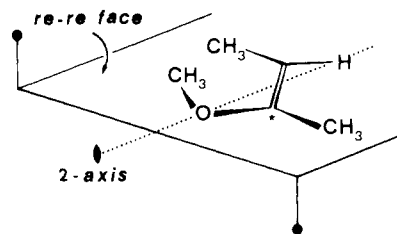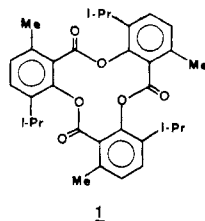

1

Figure 1. Idealized view of an orientation of the guest molecule **2** relative to the crystallographic 2-fold axis within the cavity of the TOT clathrate (**1**). Only the planar conformer is shown. The dissymmetric environment is schematized by the two symmetrically equivalent points associated with the mean olefinic molecular plane.

As suitable, prochiral guest molecules, (*Z*) and (*E*)-2-methoxybut-2-enes (**2** and **3**) where chosen. These enol ethers readily undergo dye-sensitized photooxygenation to give allylically rearranged hydroperoxides. The *E* isomer **3** gives two different racemic hydroperoxides **4** and **5**, whereas the *Z* isomer gives just

2 Z → **4 100%**

3 E → **4 66%** + **5 33%**
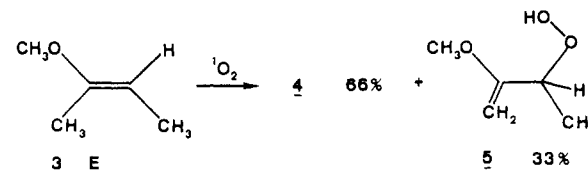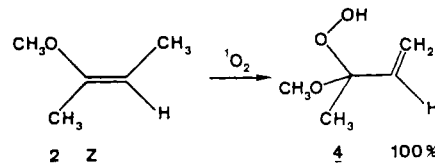
hydroperoxide **4** as a pair of enantiomers (**4**-*S* and **4**-*R*). Moreover, both enol ethers **2** and **3** form crystalline clathrates with tri-*o*-thymotide (**1**). However, the *E* isomer **3** gave achiral, triclinic crystals. Fortunately, the more tractable *Z* isomer **2** furnished *chiral*, trigonal crystals having space group *P*3$_1$21, *a* = 15.562 (1) Å, *c* = 30.383 (3) Å; *Z* = 6.

Crystals of opposite handedness were separated from the clathrate **1/2** by sorting single crystals manually and by assigning their chirality from polarimetric measurements made on small chips. Two samples of 100% optically pure clathrate (**1/2**) were so obtained and assigned the *P*-(+) and *M*-(−) configurations[6,7] by X-ray analysis.[8,9] The clathrate is of the cage type, having

(1) Morrison, J. D.; Mosher, H. S. "Asymmetric Organic Reactions"; Prentice-Hall: Englewood Cliffs, NJ, 1971. Izumi Y.; Tai, A. "Stereodifferentiating Reactions, The Nature of Asymmetric Reactions"; Academic Press: New York, 1977. Kagan, H. B.; Fiaud, J. C. *Top. Stereochem.* **1978**, *10*, 176–285. ApSimon, J. W.; Seguin, R. P. *Tetrahedron,* **1979**, *35*, 2797–2842. Valentine, D.; Scott, J. W. *Synthesis* **1978**, 329–356.

(2) Moradpour, A.; Nicoud, J. F.; Balavoine, G.; Kagan, H. B.; Tsoucaris, G. *J. Am. Chem. Soc.* **1971**, *93*, 2353–2354. Bernstein, W. J.; Calvin, M.; Buchardt, O. *J. Am. Chem. Soc.* **1972**, *94*, 494–498.

(3) Elgavi, A.; Green, B. S.; Schmidt, G. M. J. *J. Am. Chem. Soc.* **1973**, *95*, 2058–2059.

(4) (a) Gerdil, R.; Allemand, J. *Helv. Chim. Acta* **1980**, *63*, 1750–1753. (b) Gerdil, R.; Allemand, J.; Bernardinelli, G. *Acta Crystallogr., Sect. A* **1981**, *A37*, C92. Arad-Yellin, R.; Green, B. S.; Knossow, M.; Tsoucaris, G. *J. Am. Chem. Soc.* **1983**, *105*, 4561–4571.

(5) Hammond, W. B. *Tetrahedron Lett.* **1979**, *25*, 2309–2312.

(6) In solution, tri-*o*-thymotide (**1**) adopts chiral, propeller-like, left-handed (*M*) and right-handed (*P*) conformations which rapidly interconvert.[7] However, cocrystallization of **1** with a suitable guest, which is the case for **2**, occurs with spontaneous resolution so that any single crystal consists entirely of **1** fixed in the *M* or *P* configuration.

(7) Downing, A. P.; Ollis, W. D.; Sutherland, I. O. *J. Chem. Soc. B* **1970**, 24.
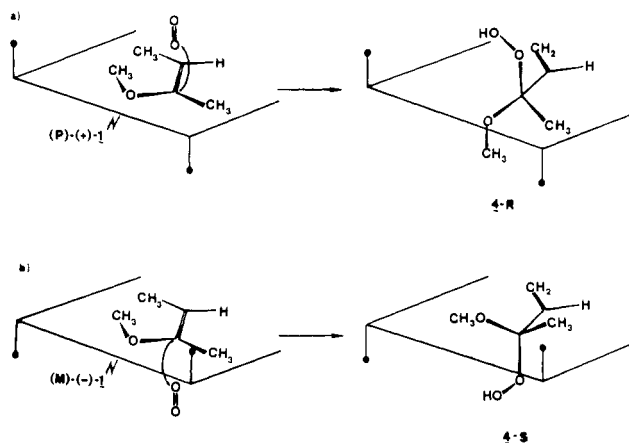
Figure 2. Attack by singlet oxygen on the *re-re* face of **2** in the (*P*)-(+)-**1** clathrate generates hydroperoxide **4** of *R* configuration (a). Development of the same nonbonded interactions requires singlet oxygen to attack the *si-si* face of the (*M*)-(-)-**1** clathrate to give **4**-*S* (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°, and -60°, respectively. The planar achiral conformation is the least populated, while the two gauche, and therefore chiral, conformations (±60°) are equally populated.

In a typical experiment, crystals of clathrate (*P*)-(+)-**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

spectroscopy,[11] whence a yield of 30% was determined for the hydroperoxide **4**. The same solution revealed by polarimetry[12] a residual optical activity of +0.060°. This experimental value corresponds to a specific rotation[13] ($[\alpha]^{20}_{546}$) of +120 ± 20° for **4**. In another experiment the clathrate of opposite configuration was used, namely, (*M*)-(-)-**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 ± 20°. 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 dissymetric 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*)-(+)-**1/2** clathrate, then **4**-*R* will be formed (Figure 2). In order that the same nonbonded interactions are developed in (*M*)-(-)-**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.

(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.

(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, [α] is calculated[13] 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$_2$C$_2$O$_2$)$_2$(H$_2$O)·4.5H$_2$O (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$_2$C$_2$O$_2$)$_2$(H$_2$O)$_3$·4.5H$_2$O are missing. They are as follows: $x = 0.28723$ (21); $y = 0.25181$ (17); $z = 0.2070$ (4).