



Fig. 1 Conformations of *cis*- and *trans*-1,2-diphenylcyclohexane-1,2-diol.

alternative conformations are equivalent. In contrast, *trans*-**3** does not have equivalent conformational energies. Since the phenyl group is larger than the hydroxy group,⁸ one would anticipate that the conformation in which the phenyl groups are equatorial would be quite a bit more stable than the conformation in which the hydroxy groups are in the axial position. This conformational preference tends to 'lock' the cyclohexanediol into the conformation with both phenyl groups in the equatorial position in the same way that the *tert*-butyl group is said to 'lock' the conformation of substituted cyclohexanes. In this conformation, the hydroxy groups are in an *anti*-relationship to each other. This expectation is consistent with molecular mechanics calculations in which the energetic difference between the conformation in which the phenyl groups are axial and the conformation in which the phenyl groups are equatorial is 5.4 kcal mol⁻¹. From this relative arrangement of groups, we conclude that either *syn*-OH groups or an antiperiplanar phenyl–OH arrangement can lead to the observed bond cleavage reactions.

The results of this study have important implications for the ferriin oxidation of *vic*-diols. A simple outer-sphere electron transfer reaction, in which an electron is transferred from the electron donor to the ferriin molecule, cannot explain the observed reactivity differences. One would anticipate that the oxidation potentials of *cis*-**3** and *trans*-**3** would be identical, since *cis*- and *trans*-1,2-diphenylcyclohexane have identical photoelectron spectra (identical ionization potentials).⁹ Our estimate of a minimum rate differential for these two compounds of 10⁴ would be inconsistent with the energetic equivalence of these two reactions.

Alternatively, one could argue that electron transfer occurs in both species, but that *trans*-**3**^{•+} is a stable species and does not lead ultimately to the dione, while *cis*-**3**^{•+} is relatively unstable and reacts rapidly to form the dione. This argument is ruled out

by two experimental results. First, there is no trace of *trans*-1,2-diphenylcyclohexane-1,2-diol in the reactions starting from the *cis*-1,2-diphenylcyclohexane-1,2-diol isomer. This argues against equilibration of *cis*-**3**^{•+} and *trans*-**3**^{•+}. Further, preliminary experimental results in which *cis*-**3**^{•+} and *trans*-**3**^{•+} were generated by single electron transfer to excited state dicyanoanthracene showed similar non-reactivity for both the *cis*- and *trans*-isomers.

The reactivity differences between *cis*- and *trans*-**3** seem to preclude reaction through a general mechanism such as that shown by the general cleavage mechanism of eqn. (2). A mechanistic interpretation that there is a sufficient energetic difference for complexation of an equatorial OH group as compared to an axial OH group is, in principle, possible. Combined with evidence that the monomethyl ethers of both *meso*- and *dl*-1,2-diphenylethane-1,2-diol are unreactive in comparison¹⁰ allows us to definitively rule out the general mechanism of eqn. (2), since two OH groups are required for the reaction.

To the best of our knowledge, such geometric requirements for the two hydroxy groups are unprecedented in the cleavage of *vic*-diols by one-electron oxidizing reagents [general oxidative cleavage mechanism shown in eqn. (2)]. We are continuing our efforts to fully understand the mechanism of this reaction in order to better understand the oxidation reaction mechanisms of one electron oxidants in reactions such as the Belousov–Zhabotinski (B–Z) reaction.^{11,12}

The geometric requirements for the ferriin oxidation of aromatic 1,2-diols involve the orientation of the two OH groups in a *syn*-position or an *anti*-periplanar phenyl–OH arrangement. The differing reactivity of **3a** and **3b** with ferriin indicates a very unexpected and unusual non-outer sphere oxidation mechanism for this type of compound.

We gratefully acknowledge the financial support of the West Virginia University Department of Chemistry.

Notes and references

- 1 R. A. Sheldon and J. K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1981.
- 2 L. W. Reichel, G. W. Griffin and A. J. Muller, *Can. J. Chem.*, 1984, **62**, 424.
- 3 H. F. Davis, P. K. Das, L. W. Reichel and G. W. Griffin, *J. Am. Chem. Soc.*, 1984, **106**, 6968.
- 4 J. H. Penn, D.-L. Deng and K.-J. Chai, *Tetrahedron Lett.*, 1988, **29**, 3635.
- 5 H. J. Penn, Z. Lin and D.-L. Deng, *J. Am. Chem. Soc.*, 1991, **113**, 1001.
- 6 J. H. Penn, A. Liu, S. Svarovsky and R. H. Simoyi, submitted.
- 7 P. J. Tomboulia, *J. Org. Chem.*, 1961, **26**, 2652.
- 8 E. L. Eliel and M. Manoharan, *J. Org. Chem.*, 1981, **46**, 1959.
- 9 S. Ruppel, PhD Thesis, Universitaet zu Koeln, 1995.
- 10 J. H. Penn, A. Liu, S. Svarovsky and R. H. Simoyi, manuscript in preparation.
- 11 Y.-C. Chou, H.-P. Lin, S. S. Sun and J. J. Jwo, *J. Phys. Chem.*, 1993, **97**, 8450.
- 12 J. Ungvarai, Z. Nagy-Ungvarai, J. Enderleihn and S. C. Mueller, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 69.

Communication 9/05728E