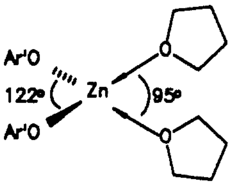

2

Clearly, the dative bonds in **2** are comparatively stronger than the dative bonds in **1**.

Dative bonds to main-group-element acceptors have sizable dipole moments and are very sensitive to inductive effects and formal charges on acceptor or donor atoms.[4] Thus, dative bonds involving main-group atoms probably have a substantial electrostatic component in general. Because Cd(II) is larger than Zn(II), it has a smaller charge-to-size ratio, a consequently weaker electrostatic interaction with THF, and thus a comparatively weaker dative bond. This electrostatic argument may apply fairly generally in such *main-group* comparisons. Exceptions are expected for extreme soft–soft interactions, and for cases with small acceptor atoms (such as boron) when dative bonds are destabilized by steric interactions between ligands.[4]

We propose that the square-planar geometry of **1** may be rationalized by identifying the Cd–O_{THF} interactions as secondary bonds. Secondary bonds were previously defined by Alcock as weak, "directed" interactions that form with 180 ± 15° angles to normal covalent bonds and are several tenths of an angstrom longer.[2] In Alcock's model, the primary bonds and lone pairs about a central atom determine the primary coordination geometry according to VSEPR, with secondary bonds forming in line with the primary bonds.[2] We submit that a distinction between the 180° interactions and other weak dative bonds is unnecessary and a more general definition is desirable; all weak interactions may serve as secondary bonds.

Thus, the geometry of **1** results from the two primary covalent bonds (aryloxide ligands) forming a linear arrangement as predicted by VSEPR for 2 coordination, and the secondary interactions (THF ligands) forming in the manner that least disrupts the primary coordination geometry. The best positions for the secondary interactions in this special case are in the clefts provided by the *t*-Bu groups, which give the observed square-planar structure. In **2**, the dative bonds are stronger and all four of the dative and covalent bonds about zinc are primary, geometry-determining bonds. Regardless of their specific natures, we suggest primary bonds be defined as those bonds that, along with the lone pairs about a central atom, dictate the primary coordination geometry, and secondary bonds as those that do not.

The principal conclusions are (1) Haaland's description of dative bonds[4] and Alcock's description of secondary bonds[2] are conceptually related and can be usefully united, (2) Alcock's definition of secondary bonds is unnecessarily restrictive, and (3) dative bonds to heavier element acceptors are comparatively weaker than dative bonds to lighter congeners when the electrostatic components of the dative interactions are dominant; the former may behave as secondary bonds and the latter as primary bonds.

Acknowledgment. Support was provided by NSF Grant DMR-8914196, and the donors of the Petroleum Research Fund, administered by the American Chemical Society. The Washington University X-ray Crystallography Facility was funded by the NSF Chemical Instrumentation Program (Grant CHE-8811456). W.E.B. thanks Professor K. G. Caulton, Indiana University, for serving as a seed crystal.

Supplementary Material Available: A description of experimental details and listings of the details of the data collection, final positional and equivalent isotropic thermal parameters, bond distances, bond angles, calculated hydrogen atom parameters, and anisotropic thermal parameters for **1** (8 pages); a listing of observed and calculated structure factors for **1** (12 pages). Ordering information is given on any current masthead page.

Conformational Enantiomers of 3,4,5,6-Tetramethylphenanthrene 9,10-Oxide. A Novel Axially Chiral Arene Oxide with Unusual Conformational Stability and Reactivity

John N. Darnow and Richard N. Armstrong*

Department of Chemistry and Biochemistry
University of Maryland, College Park, Maryland 20742

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Recent investigations of the structure and conformational stability of 3,4,5,6-tetramethylphenanthrene (**1**)[1] and the corresponding 9,10-disubstituted-9,10-dihydrophenanthrenes[2] suggested that it should be possible to prepare the strained, axially chiral conformational enantiomers of 3,4,5,6-tetramethylphenanthrene 9,10-oxide, **2M** and **2P**. The severe nonbonded interaction between the methyl groups at the 4- and 5-positions was anticipated to (i) increase the solvolytic reactivity of the oxirane by distortion of the ground state toward the geometry of the carbocation intermediate,[3] (ii) prevent the mutarotational interconversion of the two possible diastereomeric carbocations,[4] and (iii) predispose each conformational enantiomer to nucleophilic attack at only one of the two diastereotopic oxirane carbons as illustrated in Scheme I. In this paper we report the synthesis and preliminary characterization of the conformational enantiomers of **2**.

Oxidation of racemic **1** with *m*-chloroperoxybenzoic acid in a two-phase system of benzene and aqueous $NaHCO_3$[5] followed by chromatography on DEAE-cellulose in a 1:1 v/v mixture of benzene/cyclohexane gave racemic **2** in 50% isolated yield. The structure of **2** was confirmed by IR, UV, high-resolution MS, ^{13}C and ^{1}H NMR spectroscopy where the chemical shifts and vicinal coupling constant of the diastereotopic oxirane protons [δ 4.36 (d, 1 H), 4.53 (d, 1 H), $^{3}J_{9,10}$ = 4.0 Hz] were particularly diagnostic.[6] Direct oxidation of **1M** and **1P** (≥90% enantiomeric purity)[1b] at 5 °C followed by workup at low temperature afforded **2M** and **2P**, respectively, with enantiomeric purities of ≥90%. Absolute configurations of the two antipodes were confirmed by the signs of the dissymmetry transitions at 230 nm in their circular dichroism spectra (Figure 1), which reflects the helical twist of the biphenyl chromophore.[2b] The axially chiral arene oxides exhibit a substantial conformational stability characterized by a rate constant for pseudorotation, $k_{inv} = 1.9 \times 10^{-4}\ s^{-1}$ at 25 °C in *n*-hexane [ΔG^{*}_{inv} = 22.5 kcal/mol, $t_{1/2}$(racemization) = 30 min]. Activation parameters obtained from the temperature dependence of k_{inv} are as follows: $\Delta H^{*} = 22.6 \pm 0.2$ kcal/mol and $\Delta S^{*} = 0.2 \pm 0.7$ eu at 25 °C. The rather low rate of pseudorotation of **2** clearly suggests that mutarotation of the two

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(4) (a) Sayer, J. M.; Yagi, H.; Silverton, J. V.; Friedman, S. L.; Whalen, D. L.; Jerina, D. M. *J. Am. Chem. Soc.* **1982**, *104*, 1972. (b) Sayer, J. M.; Whalen, D. L.; Friedman, S. L.; Paik, A.; Yagi, H.; Vyas, K.; Jerina, D. M. *J. Am. Chem. Soc.* **1984**, *106*, 226. The interconversion of the two carbocations is also possible by the trivial re-formation of the oxirane from the zwitterionic intermediate. Ukachukwu, V. C.; Blumenstein, J. J.; Whalen, D. L. *J. Am. Chem. Soc.* **1986**, *108*, 5039.

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(6) Details of the synthesis and spectral characterization of **2**, **3**, and **4** are given in the supplementary material.

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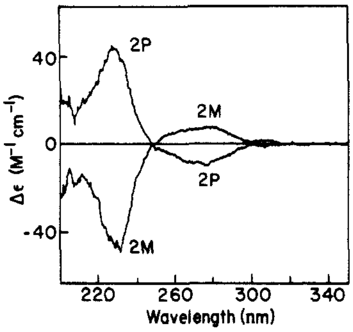
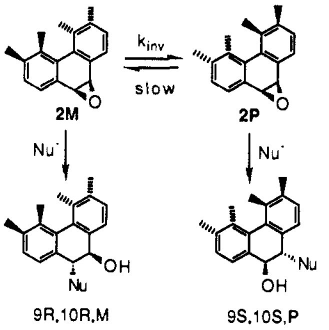
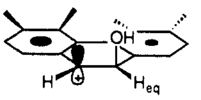


Figure 1. Circular dichroism spectra of the two conformational enantiomers of **2** at 0 °C in *n*-hexane. Activation parameters for inversion of configuration were derived from the temperature dependence of the decay of the CD transition at 230 nm.

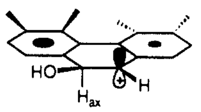
Scheme I



possible diastereomeric carbocations A and B will be slow relative to the lifetime of the intermediates.



A



B

The hindered arene oxide, **2**, is considerably more sensitive to acid-catalyzed isomerization and solvolysis than the less strained 2,3,6,7-tetramethylphenanthrene 9,10-oxide (**3**).[7] Solvolysis and rearrangement of **2** follows the rate law, $k_{obs} = k_0 + k_a[H_3O^+]$, with $k_a = (2.3 \pm 0.1) \times 10^3$ M^{-1} s^{-1} and $k_0 = (3.8 \pm 0.5) \times 10^{-4}$ s^{-1}. In contrast, **3** solvolyzes more slowly under the same conditions with $k_a = (4.8 \pm 0.1) \times 10^2$ M^{-1} s^{-1} and $k_0 = (2.0 \pm 0.1) \times 10^{-5}$ s^{-1}. Product distributions are essentially invariant with pH but differ markedly between the two isomers. Thus, solvolysis of **2** at pH 4, 7, and 10 gives 13–15% cis-dihydrodiol, 47–53% trans-diaxial-dihydrodiol, and 34–40% ketone whereas **3** yields 0.7–2.0% cis-dihydrodiol, 2.6–5.4% trans-diaxial-dihydrodiol, and 93–97% phenol. The larger amount of the trans solvolysis product from **2** at the expense of the NIH-shift product must derive in part from formation of the conformationally stable carbocation A (or its zwitterionic equivalent) with a pseudoaxial hydroxyl group that favors axial capture by solvent[8] and from which transfer of the pseudoequatorial hydride to form ketone is unlikely.[4a,9] The ratio of the NIH-shift product and cis-dihydrodiol (products that are expected to arise only from carbocation B) varies from ca. 50:1 in the solvolysis of **3** to about 3:1 with **2**.[10] This suggests that the partitioning of this carbocation conformer to either ketone or cis-dihydrodiol is controlled to some extent by nonbonded interactions between the methyl groups at the 4- and 5-positions of **2**, which would tend to favor the less strained fully sp^3-hybridized product.

As anticipated, complete transfer of chirality from the starting material to products is observed (Scheme I) under conditions where solvolysis or nucleophilic opening of **2** is much faster than pseudorotation ($k_{obs} \gg k_{inv}$). For example, all solvolysis products derived from **2M** at pH 4 exhibit an enantiomeric purity (≥90%) that is indistinguishable from that of the hydrocarbon used to prepare **2M**.[11] In addition, the specific-base- or enzyme-catalyzed (glutathione *S*-transferase) addition of glutathione to **2M** or **2P** occurs stereospecifically with trans addition of the nucleophile to the oxirane carbon of *S* absolute configuration in the M antipode and to the *R* configured carbon of the P isomer. The unusual properties of the conformational enantiomers **2** are expected to be of considerable help in understanding the solution chemistry and enzyme-catalyzed reactions of arene oxides.

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Supplementary Material Available: Description of the synthesis and spectroscopic characterization of compounds **2**, **3**, and **4** (5 pages). Ordering information is given on any current masthead page.

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(7) Kinetics of solvolysis were followed at 255 nm in 25% CH_3CN/H_2O between pH 4 and 11 at 15 °C essentially as described by Whalen et al.[3g] Products were analyzed by HPLC as previously described.[1b] The positional isomer **3** was chosen as the reference compound for **2** to minimize the expected inductive effect of the methyl groups on the reaction. The inductive effect is obviously significant as judged from comparison of the rate constants above for solvolysis of **3** at 15 °C in 75% H_2O to those of phenanthrene 9,10-oxide [$k_a = (1.15 \pm 0.09) \times 10^2$ M^{-1} s^{-1}, $k_0 = (2.5 \pm 0.2) \times 10^{-5}$ s^{-1}] at 30 °C in 100% H_2O.[3g]

(8) Trans-dihydrodiol could also arise from equatorial trapping of carbocation B by solvent. However, this unlikely possibility would lead to the conformational diastereomer with quasidiequatorial hydroxyl groups,[2a] which is not observed.

(9) Nobes, R. H.; Rodwell, W. R.; Bouma, W. J.; Random, L. *J. Am. Chem. Soc.* **1981**, *103*, 1913.

(10) Preliminary experiments in $H_2{}^{18}O$ at pH 4 indicate that the cis-dihydrodiol is derived largely (>90%) if not exclusively from axial capture of carbocation B and that <10% of this product can be attributed to equatorial capture of conformer A.

(11) Solvolysis products were separated by reversed-phase HPLC after reduction of the ketone to the corresponding alcohol with $NaBH_4$ essentially as described by: Sayer, J. M.; Grossman, S. J.; Adusei-Poku, K. S.; Jerina, D. M. *J. Am. Chem. Soc.* **1988**, *110*, 5068. The enantiomeric purity of each product was determined by HPLC on a chiral stationary phase of (+)-poly(triphenylmethyl methacrylate).[1b] The diastereomeric glutathione adducts of **2M** and **2P** were quantified by reversed-phase HPLC following: Cobb, D.; Boehlert, C.; Lewis, D.; Armstrong, R. N. *Biochemistry* **1983**, *22*, 805.

Oxidation of Primary Alcohols to Carboxylic Acids Made Easy at Iridium

Claudio Bianchini,* Andrea Meli, Maurizio Peruzzini, and Francesco Vizza

Istituto per lo Studio della Stereochimica ed
Energetica dei Composti di Coordinazione
CNR, Via J. Nardi 39, 50132 Firenze, Italy

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The oxidation of primary alcohols to carboxylic acids has no precedent for η^2-dioxygen metal complexes.[1]

In this communication we report on the synthesis and characterization of the peroxo complex [(triphos)IrCl(η^2-O_2)] (**1**), which transforms primary alcohols into carboxylic acids [triphos = $MeC(CH_2PPh_2)_3$]. Compound **1** is prepared as yellow, air-stable crystals by bubbling O_2 for 20 min through a CH_2Cl_2 (50

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