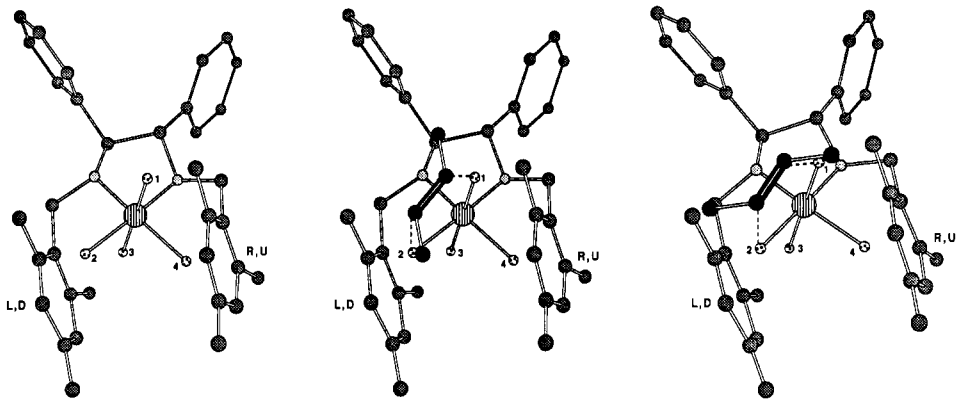

Figure 1. Left panel: complex of OsO_4 and diamine **2**; mesityl group at left projects downward, LD, and mesityl group at right projects upward, RU. Center panel: *si,si* face of (*E*)-2-butene approaching O(1) and O(2) of OsO_4·**2** complex. Right panel: *re,re* face of (*E*)-2-butene approaching O(1) and O(2) of OsO_4·**2** complex.

indicates no obstacles to the [3 + 2] pathway. Further, it is assumed that, in the transition state for cycloaddition, the geometry of the ligand approaches a C_2 symmetric structure in which there is staggering of the substituents about the N–CH_2Ar bond and placement of the mesityl groups so as to minimize steric repulsion with the nearby phenyl and Os=O substituents on the chelate ring, as shown in the left panel of Figure 1, which depicts one view of the C_2 complex. We also propose that, in the [3 + 2] cycloaddition to C=C, one of the oxygens attaching to carbon is axial and the other is equatorial to the chelate ring. This condition, which seems chemically logical since the equatorial oxygens (O(2) and O(4)) should be electron rich (electron donation from N to σ^* of trans Os–O) relative to the axial oxygens (O(1) and O(3)), provides the distinction between the four oxygens that is essential to the phenomenon of high enantioselectivity. It also provides a basis for understanding the acceleration of olefin dioxyosmylation resulting from complexation of OsO_4 with **2**, since the complex allows concerted, synergistic attack on the olefin by one relatively *electrophilic* and one relatively *nucleophilic* oxygen, in a process in which osmium is throughout six-coordinated and octahedral. The mechanistic model leads to an unambiguous prediction of absolute enantioselectivity, which is in full accord with the data in Table I.

Attack by an olefin at O(2) and O(3) is totally blocked by one mesityl group (LD; left, down in Figure 1), as is attack at O(1) and O(4) by the other mesityl (RU; right, up in Figure 1). Therefore, O(1) and O(2) and the equivalent pair O(3) and O(4) represent a unique reactivity site for attack by the olefin. Shown in Figure 1 are assemblies in which the complex is becoming attached at O(1) and O(2) to the *si,si* face (center panel) or the *re,re* face (right panel) of (*E*)-2-butene (black atoms). Attack by O(1) and O(2) on the *si,si* face of the olefin is sterically favorable since the olefin fits nicely into a groove between the mesityl groups without serious repulsion; this geometry leads to the observed major enantiomeric diol from the olefins listed in Table I. Dioxyosmylation at the *re,re* face of the olefin, in contrast, involves severe steric repulsion between the olefin and the mesityl groups, as is clear from Figure 1, right panel. Thus, the mechanistic model leads to an unambiguous prediction of the absolute configuration of the 1,2-diol products that accords with the experimental results. It should be noted that the intermediate osmium(VI) diol complex that is postulated as the primary [3 + 2] cycloadduct may undergo isomerization to a structure with two axial Os=O linkages and diol and diamine chelate rings roughly coplanar, a geometry that has been observed in known crystalline Os(VI) glycol esters.[3b,14] A mechanistic model in which olefin is attacked by the in-plane oxygens O(2) and O(4) (Figure 1, left panel) leads to an incorrect prediction of reaction stereochemistry.

The mechanistic model proposed above also provides a clear and simple explanation of the results obtained with the other effective bidentate chiral ligands that have been studied by Tomioka[3] and Hirama.[6] In addition, our model predicts lower enantioselectivity in the hydroxylation of *Z*-1,2-disubstituted and trisubstituted olefins, which is also in accord with our experimental data. For example, the following olefins were hydroxylated by the complex of **2** with OsO_4 with the indicated enantioselectivity: 1-phenylcyclohexene (60% ee); methyl (*R*)-cyclohex-3-ene-1-carboxylate (50% de); methyl 6-methyl-5-heptenoate (67% ee); (*S*)-citronellol benzoate (76% de). However, on the basis of the mechanistic model, it should be possible to devise a catalytic ligand that will be more effective for substrates such as these.

In summary, we have described a system for the enantioselective hydroxylation of *E* olefins that is unsurpassed in terms of enantioselectivity, ready availability and recoverability of the chiral controller ligand,[15] and recoverability of osmium, and we have presented the first clear mechanistic model for understanding enantioselective dioxyosmylation of olefins.[16]

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(15) In either enantiomeric form; the antipode of **2** provides products opposite in absolute configuration to those listed in Table I. The *N,N'*-bis-(benzyl) analogue of **2** was not an effective controller due to greater rotational flexibility.

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Generation and Reactivity of the 1-Nitrocyclopropyl Anion

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Cyclopropyl anions have been a popular subject of study for physical organic chemists for many decades.[1] While cyclopropane is more acidic than propane,[2] nitrocyclopropane, cyclopropyl phenyl ketone, and cyclopropyl phenyl sulfone are less acidic than their acyclic counterparts.[3] These anions also exhibit novel reactivity. Particularly striking is the report by Seebach and co-workers that deprotonation of nitrocyclopropane (pK_a = 26.9 in DMSO)[4] followed by addition of an electrophile does not result in capture of the nitrocyclopropyl anion. Instead, only coupled products result.[5] Herein we report our results on the successful

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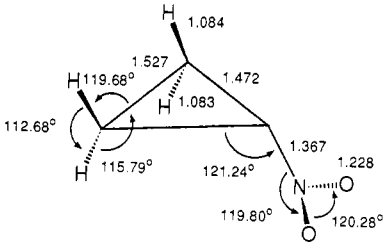
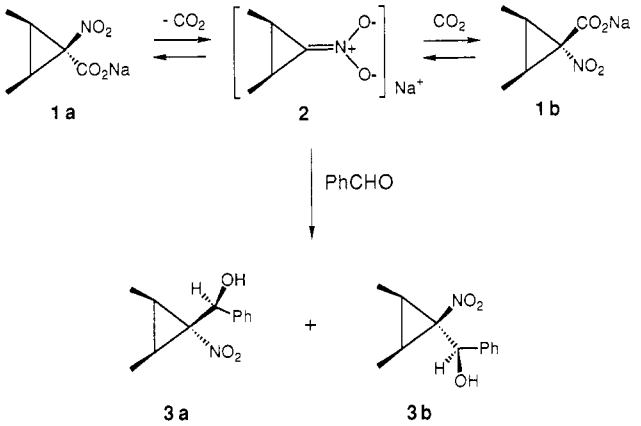


Figure 1. HF/6-31G* optimized structure for the 1-nitrocyclopropyl anion (C_s). Bond lengths are in angstroms.

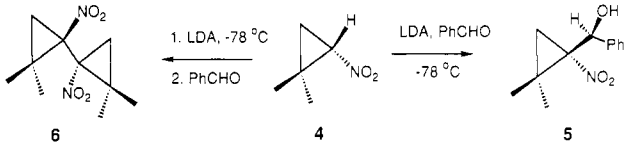
generation and trapping of the 1-nitrocyclopropyl anion as aldol adducts using two different methods.

We have recently reported that the sodium salts of 1-nitrocyclopropanecarboxylic acids (**1**), which are prepared by the saponification of ethyl 1-nitrocyclopropanecarboxylates,[6] undergo decarboxylation in wet dimethyl sulfoxide (DMSO) to produce nitrocyclopropanes in almost quantitative yield.[7] We now report



that the putative intermediate, the 1-nitrocyclopropyl anion (**2**), may be trapped[8] as nitroaldol adducts (**3**) in yields of 50–80% when the decarboxylation reaction is carried out in anhydrous 1:1 v/v DMSO/benzaldehyde solution at temperatures between 40 and 80 °C. For instance, heating such a solution of either **1a** or **1b** at 80 °C for 1 h produces a 2:1 ratio of **3a**/**3b** in 70% combined yield.[9] Other alkyl and aryl derivatives of **1** behave similarly. Remarkably, *no carbon dioxide is observed in the absence of a suitable electrophile.* However, the nitrocyclopropyl anion is almost certainly formed in low concentration under these conditions but recombines with the liberated carbon dioxide. This reversible formation of the 1-nitrocyclopropyl anion can be demonstrated by warming an anhydrous DMSO-d_6 solution of pure **1a** or **1b** to 80 °C for 1 h and examining the ^1H and ^{13}C NMR spectra of the mixture. Regardless of which isomer is used, a 3:1 equilibrium mixture of **1a**/**1b** results. There is no evidence for any dimer formation under any of these conditions. Presumably the nitrocyclopropyl anion is formed in such a low equilibrium concentration that dimerization is kinetically unfavorable.

While ethyl and methyl cyclopropanecarboxylates undergo self-condensation rather that alkylation under standard deprotonation/alkylation conditions,[10] methyl cyclopropanecarboxylates substituted by groups on both sides of the ring undergo alkylation without difficulty.[11] We have found that nitrocyclopropanes behave similarly. For example, 2,2-dimethyl-1-nitrocyclopropane (**4**), when added to a stirred solution of lithium



diisopropylamide (LDA) and benzaldehyde at −78 °C, affords the nitroaldol adducts **5** as a 10:1 mixture of diastereomers in 51% yield. The same aldol adducts **5** are obtained in 80% yield as a 5:2 diastereomeric mixture when the appropriate sodium carboxylate **1** is heated in a DMSO/benzaldehyde solution. However, this more hindered anion is still extremely susceptible to dimerization under the LDA conditions, for if the anion is generated first at −78 °C and then is quenched by benzaldehyde, only dimer **6** is obtained. Likewise, if methyl substituents are present on only one side of the ring, only dimers are obtained under all conditions.

As a further guide, we have carried out ab initio calculations[12] on the parent nitrocyclopropyl anion. At the HF/6-31+G*//6-31G* + ZPE level, the anion prefers a nonplanar C_s geometry (Figure 1) by 2.1 kcal/mol over the planar C_{2v} structure. At the minimum energy geometry, the barrier to rotation of the nitro group is 11.9 kcal/mol. Other cyclopropyl anions have also been shown to be bent.[13] Proton transfer from nitromethane to the 1-nitrocyclopropyl anion is predicted to be exothermic by 14.0 kcal/mol. This amounts to a difference in acidity of 10.3 pK_a units, in excellent agreement with the experimental results.[14] Previous workers[5] have attributed the ease of dimerization of the nitrocyclopropyl anion to a triplet ground state, and this received qualified support by nonoptimized STO-3G calculations.[15] However, our results at the ROHF/6-31+G*//6-31G* level indicate that the triplet state of the nitrocyclopropyl anion lies 29 kcal/mol higher in energy than the singlet ground state.

In conclusion, we have demonstrated that compounds **1** are efficient thermal sources of aldol adducts of variously substituted nitrocyclopropyl anions in solution. Nitrocyclopropyl anions may also be trapped from 2,2-disubstituted nitrocyclopropanes by using LDA in the presence of an electrophile. Further studies on the nitrocyclopropyl anion with regard to experimental verification of its nonplanar nature are in progress.

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Supplementary Material Available: General experimental procedures, spectral data for compounds **3a**,**b**, **5**, and **6**, and ab initio optimized geometries and energies for the singlet and triplet states of the 1-nitrocyclopropyl anion (4 pages). Ordering information is given on any current masthead page.

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