$^{31}P\{^1H\}$ NMR spectra and listings of atomic coordinates, thermal parameters, bond lengths and angles, and structure factors (21 pages). Ordering information is given on any current masthead page.

On the Mechanism of Thermal Rearrangement of (Bicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum

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Much effort has been devoted to changing the reactivity patterns of hydrocarbons by complexing them to transition metals.[1] Generally, this change is believed to occur by selective acceleration of one pathway through direct involvement of the metal in bond-cleaving and/or bond-forming processes. It has not been widely recognized that reactivity patterns can also be changed by selective inhibition of one or more pathways. The rearrangement of (bicyclo[6.1.0]nona-2,4,6-triene)tricarbonylmolybdenum (**1**) is, we believe, an example of such a phenomenon.

Thermal rearrangement of **1** to (bicyclo[4.2.1]nona-2,4,7-triene)tricarbonylmolybdenum was first reported by Grimme[2] and depicted as shown in Figure 1. However, our X-ray crystallographic analysis[3] shows that the starting material has a syn cyclopropane ring rather than the anti stereochemistry proposed by Grimme (Figure 2).[4] If migration occurred from this geometry, the product complex would have an exo-η^4 coordination of the hydrocarbon. However, it could presumably attain the final structure by intermolecular exchange, a process that can be shown to be very facile in the η^2,η^4-bicyclo[4.2.1]nonatriene)tricarbonylmolybdenum under the reaction conditions.

The following data were gathered for the rearrangement. The reaction rate was found to be cleanly first order[3] with activation parameters $\Delta H^{\ddagger} = 27.69 \pm 0.02$ kcal/mol and $\Delta S^{\ddagger} = -7.8 \pm 0.4$ cal/(mol K) between 72.9 and 125.6 °C in cyclohexane solution. Deuterated reactant[3] **1**-d_2 gave the product with the label distribution shown in Figure 3. The amount of deuterium (the total being defined as 200%) at each of the minor sites (C3 + C4 and C7 + C8) varied from 4.6% at 125 °C to 8.3% at 185.7 °C but was always equal at the two chemically distinct positions, within experimental error. Starting material recovered from a partial reaction (105.0 min at 125.9 °C) had 168.3% of the deuterium at C1 + C8, 28.9% at C2 + C7 and 2.8% at C3 + C6. Resubmission of the product to the reaction conditions did not cause further isomerization. Stereospecific labeling at C9 showed that there was concentration-dependent epimerization of the starting material, presumably caused by exchange of the ligand with traces of free hydrocarbon, which is known to epimerize very rapidly under these conditions.[5] This process could be prevented from interfering seriously by running the reaction at low concentration. It could then be determined that the bicyclo[4.2.1]nonatriene complex was formed with essentially complete retention of configuration[6]—the small amount of apparently inverted product (Figure 3) really being due to epimerization of the reactant. In contrast, the process that shifted the labels around the ring in the reactant could be shown to occur with complete inversion of configuration at the migrating methylene.

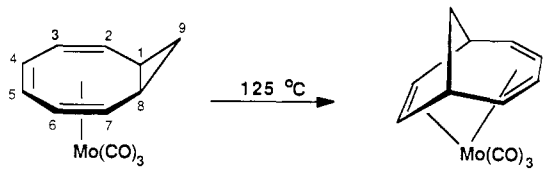

Figure 1. Original proposal for the rearrangement of (bicyclo[6.1.0]-nonatriene)tricarbonylmolybdenum.

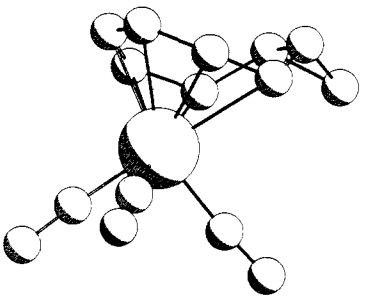

Figure 2. Computer-generated perspective drawing of (bicyclo[6.1.0]-nonatriene)tricarbonylmolybdenum from the X-ray crystal structure. Hydrogens are omitted for clarity.

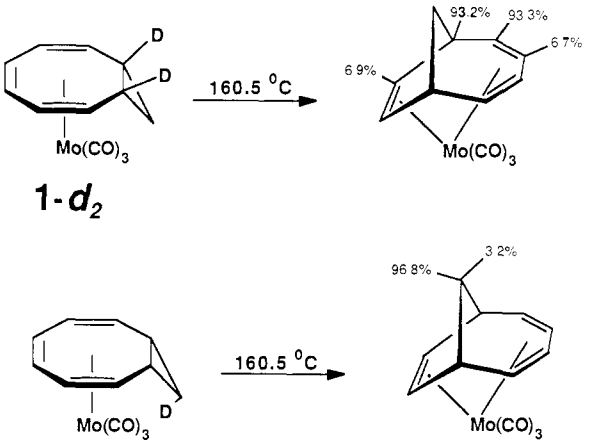

Figure 3. Deuterium distribution in the product from rearrangement of labeled (bicyclo[6.1.0]nonatriene)tricarbonylmolybdenum.

The following conclusions can be drawn from these data. (1) The rearrangement occurs within the coordination sphere of the metal since the free hydrocarbon undergoes only epimerization[5] and conversion to *cis*- and *trans*-8,9-dihydroindenes.[7,8] (2) Both epimerization and conversion to the dihydroindenes are inhibited by complexation to the metal since the activation enthalpy for rearrangement of the hydrocarbon[2] is lower than that for the rearrangement of the complex. (3) The negative activation entropy rules out the possibility of CO dissociation in the rate-determining step.

The migration of label around the eight-membered ring could be explained by a mechanism like that in A of Figure 4 with the mechanistic rate constants having relative magnitudes $k_3 >> k_0 \simeq k_5 > k_r$ (exact values depending on the temperature, of course), but microscopic reversibility prohibits inversion of configuration at C9 in this mechanism. This problem could be avoided if the methylene group became completely disconnected from the eight-membered ring as in B of Figure 4, but the label distribution in recovered **1**-d_2 eliminates such a mechanism. Since the degenerate rearrangement does occur with inversion at C9, it apparently must be a single-step [1,7] shift that does not involve the metal in direct C–C cleavage. Such a reaction is known for substituted bicyclo[6.1.0]nonatrienes.[9]

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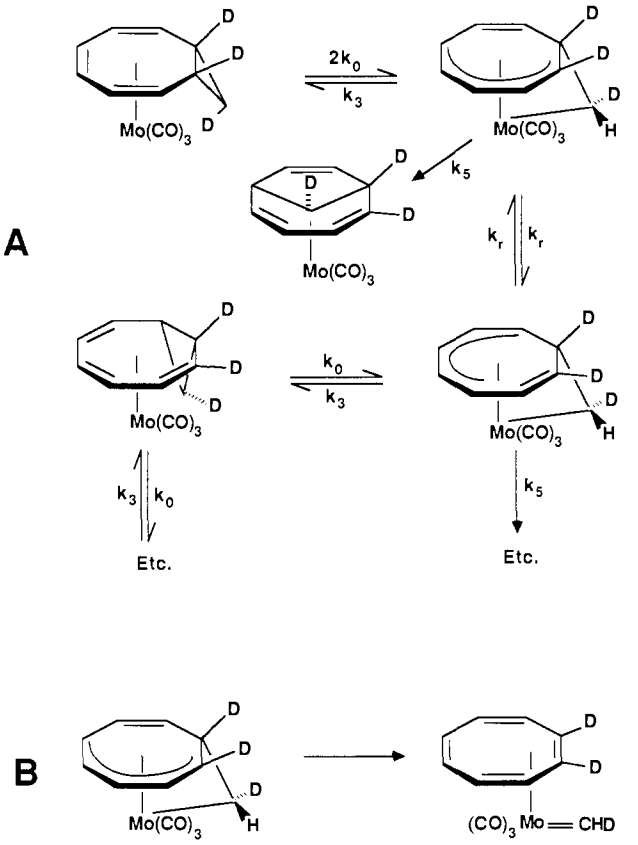

Figure 4. Mechanisms considered for label migration around the eight-membered ring. These mechanisms are rigorously excluded for the degenerate rearrangement and disfavored, but not rigorously excluded, for product formation.

The bicyclo[4.2.1]nonatriene is formed with retention of configuration at C9, and so it *could* arise from direct involvement of the metal in C–C cleavage. However, since the same bond must be broken for the degenerate [1,7] shift and for this process, it seems more economical to suppose that neither process involves oxidative addition to the metal. This view is further supported by the observation that Cr, Mo, and W complexes rearrange with rate constants that differ by a factor of only 12.6 at 111.1 °C (k_{Cr}/k_{Mo} = 5.80, k_{Mo}/k_{W} = 2.18). One might have expected a greater range of rates for oxidative addition, especially between the first- and second-row metals. Furthermore, the [1,5] shift that one would have to invoke for the reaction without direct oxidative addition is again known for substituted bicyclo-[6.1.0]nonatrienes, although it exhibits a slight preference for inversion of configuration in the one case where the stereochemistry has been studied.[10]

In summary, the degenerate [1,7] shift observed in (bicyclo-[6.1.0]nonatriene)tricarbonylmolybdenum is a process that definitely does not involve the metal in C–C cleavage. The most economical explanation of the overall rearrangement process is that complexation to the metal suppresses the epimerization and conversion to dihydroindene observed for the free hydrocarbon and thereby allows access to the higher energy [1,7]- and [1,5]-sigmatropic migrations, which occur without direct assistance from the metal.

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Functionalized Nitrogen Atom Transfer Catalyzed by Cytochrome P-450[1]

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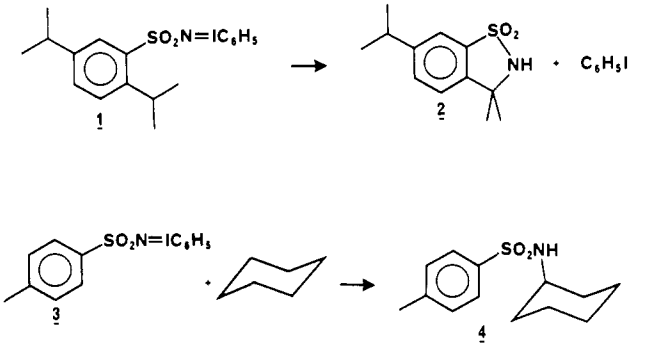
The cytochromes P-450 are heme iron-containing enzymes that catalyze NADH- and O_2-dependent substrate hydroxylations, olefin epoxidations, heteroatom dealkylations, and oxidations,[3] as well as NADH-dependent reductive dehalogenations.[4] The activation of molecular oxygen via an iron–oxene intermediate with subsequent oxygen transfer to substrate has been implicated in the P-450 reaction mechanism.[3] P-450 is also able to utilize oxygen atom donors such as iodosobenzene[5] and tertiary amine oxides[6] for substrate oxygenation. Groves and others have reproduced this latter process with metalloporphyrin model systems.[7] Recently,[8,9] metalloporphyrins have been shown to catalyze the transfer of a functionalized nitrogen atom from a tosylimide analogue of iodosobenzene (**1** → **2**; **3** → **4**). The latter reaction



has been attempted using cytochrome P-450-LM2 as the catalyst, but cyclohexanol was found as the only product.[10] We wish to report the successful cytochrome P-450 catalyzed transfer and incorporation of a functionalized nitrogen atom into a C–H bond. This enzymatic activity, previously unobserved with P-450 or any other hemoprotein, has also been found to be isozyme-dependent.

Using purified rabbit liver microsomal cytochrome P-450-LM3,4[11,12] as the catalyst, we have studied the intramolecular transfer of nitrogen in [[(2,5-diisopropylphenyl)sulfonyl]imi-

(1) Presented in part at the Sixth International Symposium on Microsomes and Drug Oxidations, Brighton, UK, Aug, 1984, and the 1984 SE Regional Meeting of the American Chemical Society, Raleigh, NC, Oct, 1984.
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