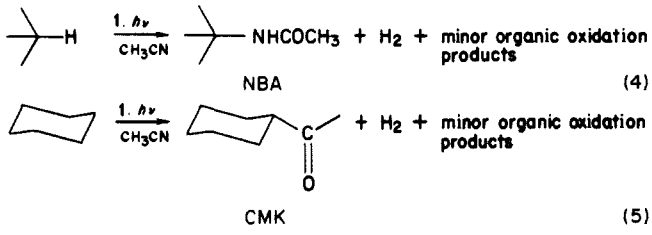
is only 1.37 ± 0.03. (4) The principal products are methyl ketone, *N*-alkylacetamide, and alkene, and the product distributions vary greatly with the alkane structure. Substrates with tertiary C–H bonds produce alkene with very high selectivities (≥90%) if the bond is adjacent to another tertiary C–H bond, *N*-alkylacetamide with very high selectivities (≥90%) if the bond is adjacent only to primary centers, as in the case of isobutane (eq 4), and a mixture of products if the bond is adjacent to at least one secondary center. All substrates with only secondary C–H bonds (cycloalkanes) yield methyl ketone; in the case of cyclohexane, cyclohexyl methyl ketone (CMK) is the only major oxidation product detectable by GC and GC/MS analysis (>90% selectivity) (eq 5)! (5) Most alkanes give little if any alcohol or dimeric coupling products (RR).




(6) For these processes, hydrogen, the only detectable reduction product, is generated in an amount approximately equal to the oxidizing equivalents represented by the organic products, providing a reasonable redox balance for the processes. (7) The quantum yields for the production of $P_{red}$ by photooxidation of alkanes are quite high (~0.1 at 350 nm) for the most reactive alkanes, and several turnovers with respect to **1** can be achieved after several hours of irradiation with the light source noted above. (8) If the reactions are run in the presence of air, typical free-radical-chain autooxidation products (e.g., alkyl hydroperoxide, ketone, or alcohol, depending on the substrate) are produced at the expense of the other products.

The low and variable ratios for reaction at secondary vs. tertiary positions, the remarkable relative rates for the various cycloalkanes, and the very low primary kinetic isotope effect all argue against C–H bond activation by rate-determining hydrogen atom abstraction (eq 6). These lines of evidence coupled with the correlation of rates with ionization potential move us to propose that at least for the linear alkanes, the substrate activation process involves an initial electron transfer; rapid deprotonation of the cation radical then produces the radical (eq 7 and 8). Elec-

$$RH + P_{ox}^* \rightarrow R^\cdot + H\text{–}P_{ox} \quad (6)$$

$$RH + P_{ox}^* \rightarrow RH^{\cdot+} + P_{red} \quad (7)$$

$$RH^{\cdot+} \rightarrow R^\cdot + H^+ \quad (8)$$

tron-transfer oxidation of strained alkanes by electrochemical methods and by photoexcited electron acceptors is well-known.[11] The most recent work on the stoichiometric oxidation of alkanes by $Co^{III}$ and related species at elevated temperatures, however, suggests that these processes probably do not involve electron-transfer oxidation of the alkane.[12,13]

Whereas the regiochemistry is likely determined by eq 7 and 8, the actual functional groups produced are dictated by the fate of the radical, R·. The production of all three types of products, methyl ketone, *N*-alkylacetamide, and alkene, is compatible with alkyl radical intermediates. The generation of methyl ketones from alkanes (e.g., eq 5), an unprecedented process for saturated hydrocarbons, likely arises by reaction of alkyl radical with acetonitrile forming an iminium radical. Subsequent hydrolysis of the imine by the few equivalents of water present then yields ketone. In contrast, the production of *N*-alkylated acetamides at tertiary positions (e.g., NBA in eq 4) is consistent only with nucleophilic capture of tertiary carbonium ion by acetonitrile followed by hydrolysis, a process analogous to the Ritter reaction. The rapid thermal oxidation of organic radicals by heteropolytungstates[14] as well as the production of *N*-alkylacetamides by electrooxidation of alkanes to carbonium ions in acetonitrile have both been reported.[15] Production of alkenes from alkyl radicals is a well-documented process.[16] In the systems reported here it is likely that alkyl radicals are generated from all alkanes but that subsequent oxidation of the radicals to the carbonium ions is important only for the readily oxidized tertiary radicals. Homogeneous alkane activation to produce radicals where only the tertiary radicals undergo subsequent oxidation to the carbonium ions competitive with capture is documented in two metalloporphyrin-based alkane functionalization systems.[6b,17]

Mechanistic and exploratory research on these new catalytic alkane functionalization processes is in progress.

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## Mechanisms of Hemin-Catalyzed Oxidations: Rearrangements during the Epoxidation of *trans*-Cyclooctene

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The epoxidations of trichloroethylene,[3] styrenes,[4] and 1-phenyl-1-butenes[3b] are accompanied by hydride or chlorine migration to produce aldehydes and ketones, respectively. These results have been variously attributed to free-radical,[3] carbocation,[4] and metallooxetane[5] intermediates. We wish to report a he-

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**Table I.** Product Yields in the TPPFeCl-Catalyzed Oxidation of Cyclooctenes by Iodosylxylene in Dichloromethane at 25 °C[a,b]

| concn[g] TPPFeCl, M | concn[g] XyIO, M | concn *trans*-cyclooctene, M | concn *cis*-cyclooctene, M | % yields[c,d] *cis*-epoxide | *trans*-epoxide | cyclooctanone[e] | cycloheptane-carboxaldehyde[f] |
|---|---|---|---|---|---|---|---|
| 0.17 | 0.04 | 0.54 | 0 | 2.4 | 45 | 0.9 | 10 |
| 0.085 | 0.04 | 0.54 | 0 | 2 | 42 | 1.1 | 10 |
| 0 | 0.04 | 0.5 | 0 | 1.1 | 0.3 | 0 | 0 |
| 0 | 0.04 | 0 | 0.54 | 0.4 | 0 | 0 | 0 |
| 0.085 | 0.04 | 0 | 0.54 | 32 | 0 | 0 | 0 |
| 0.085 | 0.04 | 0.54 | 0.54 | 4 | 33 | 1.3 | 8 |

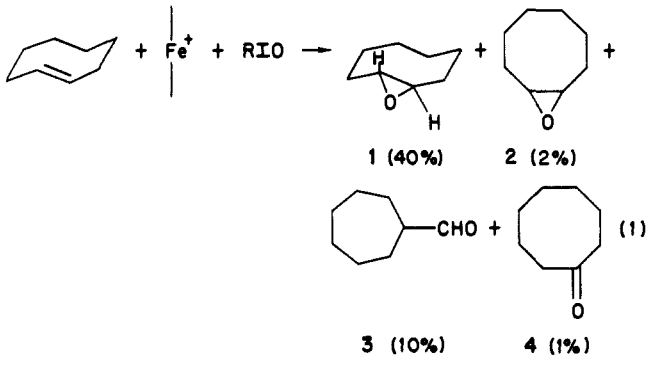
[a] Results similar to those in the first line were also obtained at 0 °C. *trans*-Cyclooctene and its epoxide were prepared by literature procedures.[6,7] [b] Reaction of *trans*-cyclooctene with *m*-chloroperbenzoic acid afforded near quantitative yield of *trans*-epoxide, less than 0.5% yield of cycloheptanecarboxaldehyde, and about 0.3% *cis*-epoxide, but no cyclooctanone. [c] Based upon the iodoxylene produced. [d] No cyclooct-2-en-1-ol[8] was formed in the catalyzed epoxidation of *cis*- and *trans*-cyclooctene. [e] Identified by retention time with an authentic sample. [f] Identified by NMR with authentic synthetic cycloheptanecarboxaldehyde.[9] [g] Neither reagent dissolved completely.

min-catalyzed oxidation which affords rearrangements that are unprecendented in free-radical chemistry and very unlikely in metallocycle chemistry.

Treatment of *cis*- or *trans*-cyclooctene with 2,4-dimethyliodosylbenzene in the presence of iron(III) tetraphenylporphyrin (TPPFeCl) afforded the products shown in Table I.

*cis*-Cyclooctene gave the *cis*-epoxide and little else. Neither *cis*- nor *trans*-cyclooctene are isomerized during the reaction and the uncatalyzed reactions do not give rearranged products. In addition, neither the *cis*- nor *trans*-epoxides give the rearranged products under epoxidation conditions. Therefore, rearranged products probably arise from some intermediate along the epoxidation pathway.

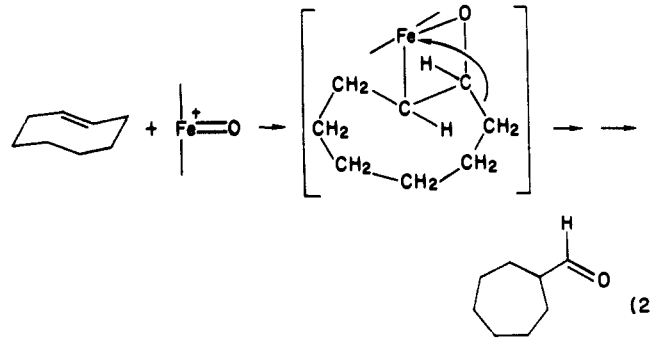
The catalyzed epoxidation of *trans*-cyclooctene, in contrast to those of other alkenes, is not completely stereospecific, giving only a 20:1 ratio of *trans*-epoxide to *cis*-epoxide. But more importantly, skeletal rearrangement occurs giving ring contraction as well as hydrogen migration. Yields are shown in parentheses in eq 1.




(1)

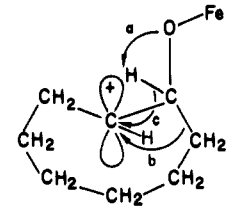
Although multiple pathways might be responsible for the incomplete stereospecificity and the rearrangements, it is also possible to explain the results with a single mechanism in which the intermediate decomposes in various ways. Importantly, unstrained alkenes such as cyclohexene or *cis*-cyclooctene do not undergo skeletal rearrangement during catalyzed epoxidation. However, hydrogen migration has been observed in the epoxidation of styrene[4] and probably occurs but has gone unnoticed in the epoxidation of other alkenes. First, since *trans*-cyclooctene gives completely stereospecific epoxidation with little or no rearrangement when epoxidized with peracids, the catalyzed reaction must differ substantially in mechanism. Some intermediate species, allowing rearrangement, is required. There are no examples of direct migration of alkyl groups in free-radical chemistry. However, both hydride and alkyl migration are common in carbonium ion chemistry.

A rearrangement might be possible in the proposed oxymetallocycle mechanism. However, the usual 1,2 elimination in such processes would, as seen in eq 2, lead to a great increase of strain rather than the strain relief required for rearrangement.



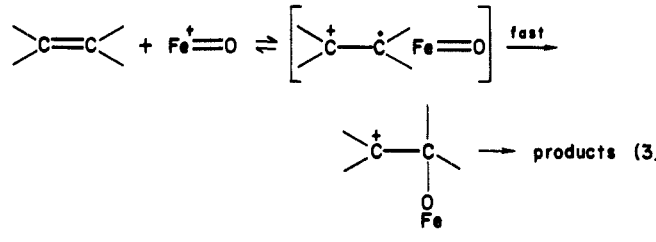

(2)

The intermediate which best explains our results is the carbocation shown below.




Simple closure (a) affords the *trans*-epoxide. Rotation about the $C_1$–$C_2$ bond leads to *cis*-epoxide. Alkyl migration (b) would be favored since this process resembles the pinacol rearrangement and also leads to relief of strain in the transition state. Hydride migration (c) does not relieve strain and little is observed. We conjecture that the usual transannular hydride migration cannot compete with pinacol-type rearrangements.

We have proposed[10b] that such carbocation intermediates arise through an electron transfer followed by cage collapse (eq 3), a




(3)

process similar to that proposed by Ortiz de Montellano for the P-450 catalyzed oxidation of quadricyclene.[5c] This mechanism implies a dependence upon the ionization potential of the alkene and thus a large difference in rates of reaction of *cis*- and trans-cyclooctene. Only a factor of 14 was observed. However, the cis/trans reactivity ratios in these catalyzed epoxidations usually range from 15 to 90.[10b] Correcting for this preference,

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the actual rate ratio for *trans*-cyclooctene to *cis*-cyclooctene would be 200–1200, closer to what might be expected for electron transfer.

Therefore, although questions remain, the electron-transfer-carbocation mechanism appears to best explain the epoxidations of reactive alkenes.

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(11) We have recently observed a small amount of cyclohexene-4-carboxaldehyde during catalyzed epoxidation of norbornene,[10b] indicating some skeletal rearrangement in that epoxidation.

## High-Resolution $^{14}N$ Overtone Spectroscopy: An Approach to Natural Abundance Nitrogen NMR of Oriented and Polycrystalline Systems

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In this paper, we present a novel approach to nitrogen NMR spectroscopy of both oriented and polycrystalline samples. The method employs the direct excitation and detection of $^{14}N$ overtone NMR transitions at approximately twice the $^{14}N$ Larmor frequency.[1]

New approaches to nitrogen NMR are needed both because of the chemical and biochemical importance of nitrogen and because of the limitations of current methods. In the solid state, $^{15}N$ NMR typically requires isotopic labeling to achieve sufficient sensitivity.[2-5] Through cross-polarization,[6] good sensitivity is achieved in $^{14}N$ NMR of single crystals. The large quadrupole interactions of $^{14}N$ nuclei provide high resolution in single-crystal spectra but at the expense of a spectral width of several megahertz.[7-16] Since the experimentally observable spectral range is only about 200 kHz, it is impossible to acquire a complete spectrum without repeated retuning of the spectrometer. $^{14}N$ powder pattern spectra have only been obtained with indirect detection[17] or when the quadrupole couplings are unusually small.[18,19] Large quadrupole couplings also limit the applicability of double-quantum[20-24] and zero-field[25-27] NMR techniques. For these reasons, we became interested in the insightful proposal by Bloom,[1a] and the experimental demonstration by Legros and Bloom,[1b] that $^{14}N$ overtone NMR transitions can be directly excited and detected in the solid state.

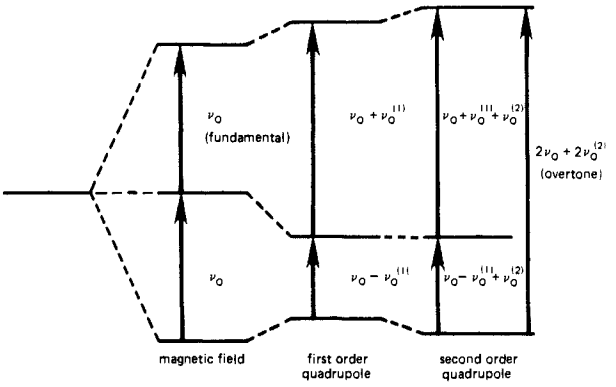


**Figure 1.** Spin energy level diagrams for $^{14}N$ NMR. In a large static magnetic field fundamental transitions at the Larmor frequency $\nu_0$ (18.06 MHz in a 5.87-T field) are observed. The first-order effect of a quadrupole coupling in the solid state is to split the fundamental spectrum into a doublet, with a splitting of $2\nu_Q^{(1)}$ (up to 4.5 MHz with $e^2qQ/h = 3.0$ MHz). For large quadrupole couplings, a second-order shift $\nu_Q^{(2)}$ (up to approximately 50 kHz) is observed in the fundamental spectrum. Overtone transitions at $2\nu_0 + 2\nu_Q^{(2)}$ become allowed and can be directly detected by pulsed NMR.

The essential physical aspects of $^{14}N$ NMR are summarized in Figure 1. In an applied magnetic field, there are three spin energy levels separated by $h\nu_0$. Since only transitions at the Larmor frequency $\nu_0$, i.e., the fundamental transitions, are allowed by dipole selection rules, a single resonance is observed. In solids and oriented systems, the quadrupole interaction effectively shifts the middle energy level with respect to the others by $\nu_Q^{(1)}$. When the quadrupole coupling constant $e^2qQ/h$ is much smaller than $\nu_0$, the fundamental spectrum becomes a doublet centered at $\nu_0$ with a splitting of $2\nu_Q^{(1)}$. As $e^2qQ/h$ becomes larger, second-order effects appear. One second-order effect is to shift the lowest energy level down and the highest energy level up by the second-order shift $\nu_Q^{(2)}$. The other second order effect, which is crucial for overtone NMR, is to make transitions between the lowest and highest energy levels, i.e., the overtone transitions, weakly allowed. Thus, a single resonance can be observed at $2\nu_0 + 2\nu_Q^{(2)}$, or approximately twice the $^{14}N$ Larmor frequency. Since the overtone frequency is only affected by $\nu_Q^{(2)}$, the total width of an overtone spectrum is less than that of a fundamental spectrum by a factor of approximately $8h\nu_0/e^2qQ$ (45 for the example shown here).

Figure 2 contains the first examples of high-resolution $^{14}N$ overtone NMR spectra obtained with proton decoupling and cross-polarization, illustrating the resolution and sensitivity of the technique. The two resonance lines in each spectrum arise from two inequivalent molecules in the unit cell of the 50-mg *N*-acetylvaline crystal. The 200-Hz line widths are approximately 10 times less than the corresponding fundamental line widths.[8] The comparison of Figure 2, parts A and B, demonstrates the signal enhancement resulting from cross-polarization using a

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