Oxidation of Alkenes in Supercritical Carbon Dioxide Catalyzed by Molybdenum Hexacarbonyl

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In supercritical CO_2, olefin oxidation to epoxides or diols using a $Mo(CO)_6$ catalyst precursor and using t-BuOOH as oxidant proceeds in nearly quantitative yields. The highest yields and fastest rates of diol and epoxide formation were observed with *cis*-alkenes, while *trans*-alkenes were considerably less reactive. Phenyl-substituted olefins show a tendency to cleave to their corresponding aldehyde. The use of 70 wt % aqueous solutions of *tert*-butyl hydroperoxide yield the *trans*-diol, while anhydrous decane solutions of t-BuOOH give the epoxide. Clearly $Mo(CO)_6$ proved to be the most effective oxygen transfer catalyst for these reactions. Several other oxygen transfer catalysts were tested but proved to be less effective under these conditions. An autoclave equipped with quartz windows allowed for the qualitative determination of a homogeneous reaction environment in the supercritical fluid.

Introduction

Metal-catalyzed oxidative transformations of olefins are fundamental to organic synthesis and have been investigated extensively for decades.[1] Elaborate kinetic and mechanistic studies,[2] large volume industrial synthesis Halcon process,[3] and, most recently, asymmetric catalyst design[4] have been developed. However the best yields and highest enantioselectivities are achieved in a restricted range of environmentally hazardous solvents such as aromatic or chlorinated compounds. Many current research endeavors are fueled by the desire to reduce the emission of hazardous waste generated by these toxic solvents. We believe that replacing these traditional systems with a more benign solvent is a feasible solution.

Conducting chemical reactions at supercritical conditions affords opportunities to manipulate the reaction environment (solvent properties) by simply adjusting the pressure and temperature of the reaction.[5] It has been shown that the density, viscosity, diffusivity, and overall solvent strength of a supercritical fluid can be dramatically varied by small changes in pressure and/or temperature.[5] A spectrum of conventional solvents ranging from pyridine to pentane can be mimicked by SC CO_2 with small variations in the temperature and pressure.[5b] Initial investigations of chemical oxidation in supercritical fluids centered around supercritical water oxidation (SCWO).[6] Destruction of organic wastes by SCWO has proven useful, but a paradigm shift was needed to view supercritical fluids (SCF's) as potential reaction media for designed chemical synthesis via partial oxidation.

Our original goal was to explore the use of SC water (H_2O: $T_c = 647.3$ K, $P_c = 217.6$ atm) as an environmentally safe solvent system for constructive organic synthesis. Indeed, Diels−Alder reactions have been carried out in supercritical H_2O with a dramatic increase in rate and yields without added catalysts.[7] Furthermore, the oxidation of alkyl aromatics to aldehydes and acids in SC H_2O has shown great promise (eq 1).[8]

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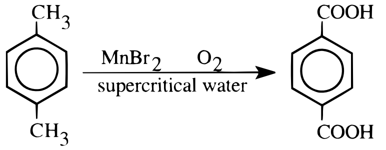
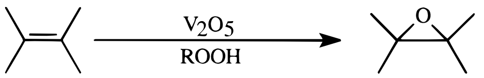


(1)

This above reaction is dependent upon $MnBr_2$ initiating a radical chain reaction to yield the oxidized product. The use of a radical-based catalyst results in limited stereoselectivity. Our focus then turned to metal-catalyzed oxygen transfer to alkenes utilizing supercritical water as a benign solvent. The oxidation of stilbene in the presence of molecular oxygen and $MoO_2(acac)_2$ or $VO(acac)_2$ was explored. Good yields of benzaldehyde and benzoic acid were attained suggesting that a radical process was still occurring.[9] Satisfactory selectivity was obtained, but the reaction was limited to thermally stable olefins and those alkenes which provided a stable benzyl radical intermediate. All other simple nonconjugated olefins (e.g. cyclohexene, norbornylene, 1-octene) decomposed in the extremely harsh environment of supercritical H_2O. The intolerance of many functional groups to supercritical water limited the scope of the process, resulting in the need for a different approach.

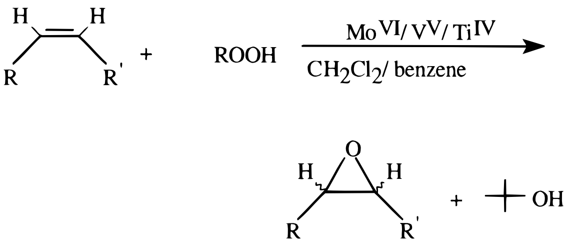
We have been encouraged by recent successful work in the milder reaction medium of supercritical carbon dioxide[10] (CO_2: $T_c = 304.2$ K, $P_c = 72.8$ atm). Not only is CO_2 an environmentally friendly solvent, it is also readily available, nonflammable, nontoxic, and practical to use in moderate pressure autoclaves. Carbon dioxide is an especially attractive solvent for catalytic oxidations because it is noncoordinating and inert toward any further oxidation. Recent success in SC CO_2 has been achieved with the asymmetric catalytic hydrogenations of olefins, as well as for various selective oxidation reactions.[11] DeSimone and co-workers have replaced organic solvents with SC CO_2 for the synthesis and processing of polymeric materials,[12] while Tanko and Blackert have also demonstrated the ability to carry out free-radical side chain bromination of alkyl aromatics in SC CO_2.[13] The relatively mild conditions of this solvent system appeared attractive for the goals of our project. Thus we began to explore supercritical CO_2 as a solvent for the epoxidation of olefins. We have recently designed a novel vanadyl(salen) catalyst[14] which has been used to achieve quantitative epoxidation of various allylic alcohols in the presence to t-BuOOH.[15]

In the 1950s, Hawkins was the first to show that alkenes could easily be converted to epoxides in the presence of alkylhydroperoxides and vanadium pentoxide (eq 2).[1j]



(2)

This work paved the road for companies such as Halcon International and Shell to patent the epoxidation of propylene to the valuable commodity propylene oxide. This reaction, known as the Halcon process, utilizes an alkylhydroperoxide and metal oxygen transfer catalysts such as molybdenum and vanadium to achieve the epoxidation of olefins (eq 3).[3] Since then, a variety of metal complexes in high oxidation states have been used in similar oxygen transfer processes.[1,2,16]



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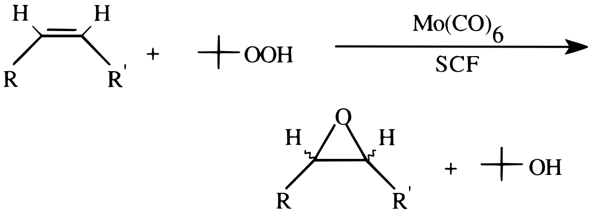
In this work we attempted to perform this important oxidation reaction in an environmentally safe solvent system. Our ultimate goal is to replace chlorinated solvents with supercritical CO_2 as a useful solvent system for the selective oxidation of organic compounds. In this paper we report the successful oxidation of alkenes to epoxides (eq 4) or diols (eq 5) using $Mo(CO)_6$



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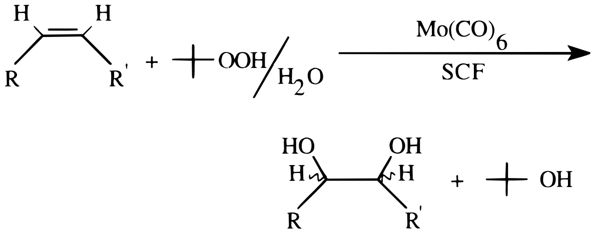

(5)

as a catalyst in supercritical CO_2. We attained clean, high-yield conversions using a relatively simple apparatus assembled from commercially available components. Thus, a new benign solvent, supercritical CO_2, successfully replaces a restricted solvent in this important reaction.

Results and Discussion

Supercritical CO_2 as a Solvent. Our initial studies in supercritical CO_2 have focused on the oxidation of

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Table 1. Oxidation Products and Yields Obtained by Using $Mo(CO)_6$ Catalyst[a] in SC CO_2[b]

entry	olefin	oxidant	ratio subs:ox	temp, °C	*t*, h	yield[c]/product
1	cyclohexene	70% aq t-Bu	1:2	95	3	100% *anti*-1,2cyclohexandiol
2	cyclohexene	70% aq t-Bu	1:1	95	3	100% *anti*-1,2cyclohexandiol
3	cyclohexene	70% aq t-Bu	1:1	80	3	47% cyclohexene oxide
4	cyclooctene	70% aq t-Bu	1:3	86	3	100% cycloocten oxide
5	cyclooctene	t-BuOOH[c]	1:3	86	3	100% cyclooctene oxide
6	norbornylene	70% aq t-Bu	1:3	92	3	66% norbornanediol
7	1-octene	70% aq t-Bu	1:3	103	4	80% 1,2-octanediol
8	*cis*-2-heptene	t-BuOOH[c]	1:3	95	3	20% 2,3-heptane oxide
9	vinylcyclohexane	t-BuOOH[c]	1:3	90	3	20% cyclohexenylethylene oxide
10	2-vinylnaphthalene	70% aq t-Bu	1:3	92	3	80% 2-vinylnaphthaldehyde
11	1-vinylnaphthalene	70% aq t-Bu	1:3	92	3	80% 1-vinylnaphthaldehyde
12	*trans*-β-methylstyrene	70% aq t-Bu	1:3	90	3	30% benzaldehyde
13	*cis*-stilbene	70% aq t-Bu	1:3	95	3	50% benzaldehyde
14	trans-stilbene	70% aq t-Bu	1:3	100	6	no reaction
15	*trans*-2-heptene	70% aq t-Bu	1:3	94	3	no reaction

[a] All reactions were run with 0.02 equiv of catalyst. [b] 3200 psi CO_2 is initially loaded into the reaction vessel at room temperature. [c] 5.0−6.0 M solution in decane.

simple olefins. Cyclohexene was our initial test system, and we found that it can be quantitatively converted to its corresponding diol under relatively mild conditions. A 316 stainless steel high-pressure reaction vessel was loaded with alkene, an aqueous solution of *tert*-butyl hydroperoxide (t-BuOOH), and $Mo(CO)_6$, charged with CO_2 to 3200 psi, and heated at 96 °C over a 3 h period. The desired temperature inside the reaction vessel was reached within 50 min of heating as monitored by an in situ thermocouple. The initial pressure of CO_2, about 3200 psi, was observed to rise to approximately 7500 psi as monitored by an in situ pressure transducer. After venting of the CO_2 from the reaction vessel through a diethyl ether reservoir over a 20 min period, an analytically pure white powder was isolated by filtration. This powder was determined to be *trans*-cyclohexanediol by GC/MS and NMR. It was weighed to give a 100% yield of oxidized product based on the alkene.

This new autoclave allows us to visually monitor the behavior of the solution during the reaction. The liquid CO_2 is added to the autoclave along with reactants and catalysts until a pressure of approximately 2500 psi is achieved. At this point a dark nontransparent emulsion forms inside the reaction vessel. By simply heating the autoclave to 35 °C and shaking in a water bath for 30 min, we observe a completely transparent homogeneous solution, confirming that the reaction is completely homogeneous.

A variety of other olefins (Table 1) were examined in order to better define the scope of this reaction. Cyclic olefins tend to give the cleanest products and best yields, while *trans*-olefins tend to give no oxidized product at all. Cyclohexene is converted to its diol in only 3 h at approximately 95 °C, while the terminal 1-octene requires longer times at higher temperatures to give 85% yield of diol. Furthermore, *cis*-2-heptene is converted to its epoxide in a much lower yield. The decrease in rate of reaction may be due to steric effects as suggested by the inability of *trans*-stilbene to undergo reaction, and the lower yield of aldehyde from *trans*-β-methylstyrene compared to the similar 2-vinylnaphthalene. The limited accessibility of the olefin to the relatively large Mo catalyst is believed to be the reason for this steric sensitivity. In the cyclic alkenes such as norbornene, cyclohexene, and cyclooctene, the alkyl groups can be viewed as "tied back", allowing for an unhindered approach to the proposed Mo−alkylperoxidic complex. The straight chain alkenes such as vinyl cyclohexene, 1-octene, and 2-heptene are more sterically hindered due to their "floppy" side chains, accounting for their more sluggish reactivity. The greater reactivity of internal olefins compared to that of 1-octene can be explained by the increased alkyl substitution. The electron-releasing alkyl groups increase the alkene's nucleophilic character, making it more reactive toward the electrophilic Mo catalyst.[2h]

It is also important to note that olefins containing phenyl substituents, such as *cis*-stilbene, *trans*-β-methylstyrene, and 2-vinylnaphthalene, give more oxidative cleavage products than the aliphatic alkenes. No traces of epoxide or diol were observed when phenyl-substituted olefins were used at these conditions, hinting that another type of mechanism may be necessary to explain these reactions. The stability of the benzyl radical observed in previous SC water reactions supports the possibility that these reactions could proceed by a radical mechanism. In addition to this, we also observed that the molybdenum catalyst can oxidize toluene to benzaldehyde (25% yield) in SC CO_2, which supports the hypothesis that a radical mechanism can operate in SC CO_2. To further test this hypothesis, the oxidation of vinylcyclohexane was investigated. It shows no cleavage products, presumably due to the inability for the cyclohexane to form a stable radical intermediate (eq 6). The absence of a cleavage product supports the idea that a radical mechanism only predominated when a phenyl group is available to stabilize a radical intermediate.

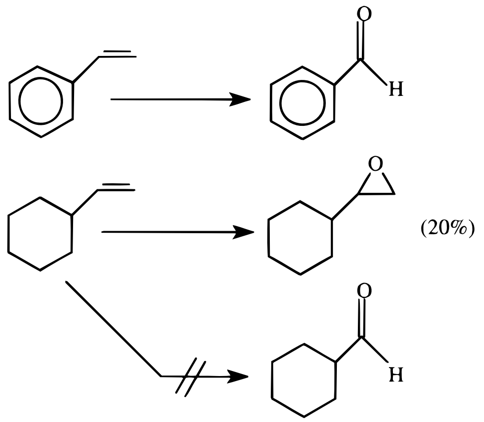

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Table 2. Catalyst Activity in SC CO_2[a]

catalyst	amt, mg	yield of diol, %
$MoO_2(acac)_2$	100	<5
$VO(acac)_2$	100	<5
$Mo(CO)_6$	100	100
$Mo(CO)_6$	200	100
$Mo(CO)_6$	50	77
$Mo(CO)_6$	0	0
$Mo(CO)_5(C_8H_{14})$[b]	100	50 (epoxide)

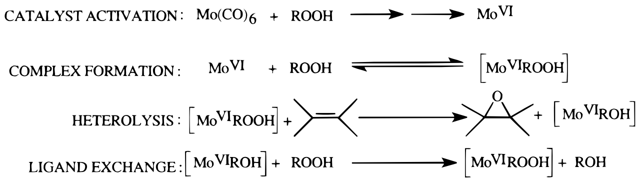
[a] All reactions used 1.5 mL of cyclohexene and 2.0 mL of t-BuOOH at 94 °C for 3 h. [b] Run at 65 °C for 90 min.

To directly compare the performance of CO_2 to those of other more conventional solvents, we oxidized cyclohexene in neat alkene and also using benzene as a solvent in the same autoclaves under the same time/temperature conditions. Reactions in these solvents did not proceed as efficiently as the SC CO_2 reactions giving only 70% and 90% yields of the diol in the neat alkene and benzene reactions, respectively. Furthermore they were not as clean as in the CO_2. Unlike the CO_2 system, a yellowish residue in the ether layer, an insoluble dark blue material *(vide infra)*, and numerous other byproducts were detected in these reactions. As an additional test, the oxidation of 2-vinylnaphthalene (solid) was tested both in SC CO_2 and neat. Starting material and a dark blue solid were deposited inside the reaction vessel when the reaction was run neat. Only 25% of 2-vinylnaphthaldehyde was recovered from this reaction while the SC CO_2 reaction gave 80% yield of pure 2-vinylnaphthaldehyde with recovery of the remaining starting material.

Choice of Catalyst. A molybdenum species is clearly involved in the oxygen transfer process as demonstrated by the lack of desired reactivity in its absence (Table 2). The molybdenum catalyst remains active at the end of the reaction and can oxidize consecutive batches of olefin. This was demonstrated by venting the reaction vessel after one batch of olefin had gone to completion, charging it with more olefin and CO_2, and allowing it to react for another 3 h at the desired temperature. High yields of epoxide were attained even after numerous rechargings indicating no loss of activity of the catalyst. Furthermore, a turnover number of at least 150 per batch was obtained for the $Mo(CO)_6$ upon optimization of the cyclohexene reaction.

Unfortunately, attempts to carry out these epoxidations with $MoO_2(acac)_2$ or $VO(acac)_2$ catalysts were unsuccessful under these reaction conditions making $Mo(CO)_6$ an important catalyst precursor.. Preliminary studies have shown a lack of catalyst solubility to be the primary problem. When an open Pyrex capillary is loaded with $Mo(CO)_6$, placed in the steel autoclave, and subjected to typical reaction conditions, the capillary is recovered completely empty suggesting that the carbonyl catalyst is solubilized by the CO_2. In contrast, the metal acetylacetonate catalysts are recovered unchanged in their capillaries, even after prolonged exposure to reaction conditions. Thus, catalyst solubility appears to be a serious limitation in this system. It has been previously observed that the most effective molybdenum catalysts contain a coordination environment of hard electronegative ligands which are stable to harsh oxidizing conditions.[16] Many molybdenum compounds have been shown to act as epoxidation catalysts, including oxides, sulfides, halides, acids, salts, and carboxylates.[16] Current work is focused on increasing the solubility of some of these catalysts in SC CO_2.

Scheme 1



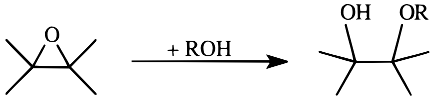
The general mechanism for the molybdenum-catalyzed epoxidation reaction has been extensively studied by other workers and can summarily be viewed as a four-step process (Scheme 1). The established mechanism is probably a reasonable approximation of what is occurring in our system, with SC CO_2 acting as a nonpolar weakly coordinating solvent. An induction period prior to any epoxidation has been observed in our work *(vide infra)* and can be explained by the first step of the proposed reaction mechanism. There is literature precedent for this induction period, in which the molybdenum catalyst is oxidized by the alkylhydroperoxide to its highest oxidation state, the active Mo^{VI}.[1,2,16] The subsequent step is a rapid and reversible reaction in which the active catalyst, which is presumably a molybdenum hydroperoxide complex, is formed. Thereafter, the intact alkylhydroperoxide complex can react with the olefin, to irreversibly form the epoxide and alcohol-substituted metal complex. Substitution of the alcohol-substituted complex by fresh hydroperoxide could re-form the active catalyst and complete the catalytic cycle.

Effect of Water on Selectivity. At temperatures below 90 °C, good yields of epoxide were observed. However above 90 °C diols were the predominant product. This inability to quantitatively produce epoxide at higher t-BuOOH concentrations is likely due to the presence of water in the alkylhydroperoxide solution, which is purchased as a 70 wt % or 90 wt % aqueous solution. This aqueous solution provides more than enough water to account for the hydrolysis of the epoxide. A mixture of 70 wt % aqueous t-BuOOH and cyclohexene oxide in SC CO_2 shows a slow transformation of epoxide to the diol over a 3 h period at reaction temperatures, but a similar experiment in CO_2 with a 5.0−6.0 M anhydrous solution of t-BuOOH in decane leads to the complete recovery of the epoxide after a 3 h period at reaction temperatures. Recent work has demonstrated that the use of pyridine could actually retard the acid-catalyzed ring opening of the epoxide to the *trans*-diol.[1b] Work is currently under way to test the effect of pyridine in the SC CO_2 solvent. The three-membered epoxide ring is very reactive toward acid-catalyzed ring opening by nucleophilic attack. The water and CO_2 generate a weakly acidic environment in which the oxygen of the epoxide can be protonated to provide a better leaving group for the subsequent nucleophilic attack of water. This mechanism suggests that the hydroxyl groups should be anti to each other, and this was confirmed by ^1H NMR of the isolated 1,2-cyclohexanediol product. In an attempt to slow the rate of epoxide hydrolysis, we dried the t-BuOOH over drying agents, but a completely dry reaction environment could not be attained in this manner, and more rigorous approaches to dry the t-BuOOH were deemed dangerous. Reaction of $Mo(CO)_6$ and cyclohexene with anhydrous t-BuOOH (5.0−6.0 M solution in decane) in SC CO_2 yields only epoxide. The absence of diol in this reaction only reinforces the hypothesis that the aqueous solution of t-BuOOH is primarily responsible for the diol products.

In addition to hydrolysis, the presence of H_2O in the system plays a second deleterious effect by slowing the rate of the reaction. The H_2O is able to compete with t-BuOOH for coordination sites on the metal. By an increase of the water content in the system, a considerable decrease in the rate of reaction was observed. Similar results were observed in the presence of excess 2-methylpropanol, which is also capable of coordinating the transition metal.

Interestingly, *cis*-cyclooctene was oxidized in 100% yield to its epoxide with no sign of hydrolysis to the diol regardless of the presence of water. An attempt to make the diol by reacting cyclooctene oxide with aqueous t-BuOOH led to no reaction at 95 °C, demonstrating that the epoxide is stable under these reaction conditions, unlike the epoxides of cyclohexene, norbornylene, and 1-octene.

Temperature Effect. Reactions run below 75 °C allowed for the complete recovery of the olefin and $Mo(CO)_6$ with no oxidation observed. But as the temperature was increased above 80 °C, the oxidation of the alkene began to take place, and the white solid $Mo(CO)_6$ was no longer recoverable. This higher temperature effect was expected on the basis of previous observations,[1,2] but an active intermediate was not isolated. When $MoO_2(acac)_2$ is used, or when $Mo(CO)_6$ is heated above 110 °C for more than 3 h, a dark blue solid forms. This blue compound is most likely a reduced molybdenum oxide cluster. The formation of this solid appears to be an undesirable thermodynamic sink in the reaction which must be carefully avoided by limiting reaction times and temperatures. The "molybdenum blue" showed no catalytic activity. In addition to the formation of molybdenum blue above 100 °C, the addition of *tert*-butyl alcohol to the epoxide increases, resulting in decreased selectivity due to solvolysis of the epoxide (eq 7).



(7)

Since there was no reactivity below 75 °C using $Mo(CO)_6$, we postulate this reaction is temperature limited by the dissociation of CO from the $Mo(CO)_6$. The synthesis of a Mo catalyst with a more labile ligand was investigated, and the compound $Mo(C_8H_{14})(CO)_5$ was easily synthesized from a known procedure[8] and used replacing $Mo(CO)_6$. Care was taken with this thermally unstable catalyst to keep it as cold as possible until the CO_2 could be loaded into the bomb, as the straw colored compound rapidly decomposes when taken out of an inert atmosphere or when warmed to room temperature. Reactions run at 65 °C with $Mo(C_8H_{14})(CO)_5$ as a catalyst gave a clean reaction with 50% yield of epoxide. This good reactivity at lower temperature strongly suggests that initial dissociation of CO is required for catalytic reactivity of the $Mo(CO)_6$ catalyst.

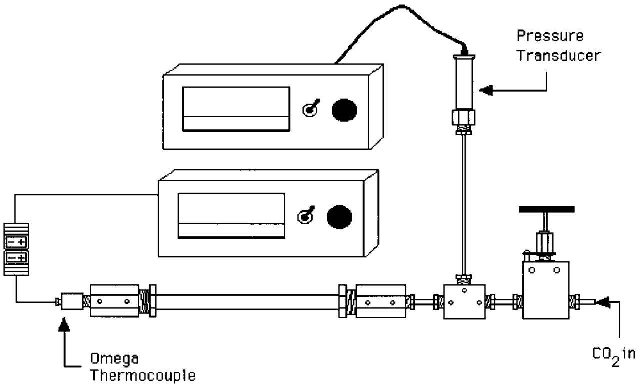


Figure 1. The reaction vessel assembled from commercially available components purchased from HiP and Omega.

Conclusions

We have shown that the oxidation of olefins to epoxides or diols in SC CO_2 proceeds efficiently, selectively, and with a wide scope using $Mo(CO)_6$ as a catalyst and organic peroxides as an oxygen source. The yields of diol are generally better in SC CO_2 compared to conventional solvents, and the products are generally much cleaner. The epoxides can be obtained under anhydrous conditions. Molybdenum has proven to be an effective oxygen transfer catalyst precursor at 95 °C, and we are currently investigating more reactive catalysts, including those capable of inducing stereoselectivity. Finally, substrates with aromatic groups adjacent to the alkene are usually oxidized cleanly to aldehydes suggesting that a radical mechanism takes place in these cases.

Experimental Section

Equipment and Instrumentation. General Comments. All reactions which utilized SC CO_2 were performed in HIP 316 stainless steel reaction vessels with standard cone and thread fittings. The vessels were assembled from simple components purchased from the High-Pressure Equipment Co. (Figure 1). These vessels have an internal volume of 10.1 mL and can withstand temperatures and pressures of 400 °C and 20 000 psi, respectively. Supercritical fluid grade carbon dioxide (99.99%) was purchased from AGA Specialty Gases and was introduced into the vessels using a high-pressure line equipped with an air-driven gas compressor from Autoclave Engineers. A Hewlett-Packard gas-chromatograph model 5890/ Hewlett Packard series mass selective detector model 5970 (at 70 eV) was used to identify products by comparison (GC retention time and mass spectra fragmentation patterns) with standard samples (Aldrich). The column used in the GC was an Alltech SE-30. Infrared spectra were obtained on a Nicolet Magna IR spectrometer model 550 while NMR data were collected on a Bruker AC-300 MHz spectrometer. Product yields were determined by one of three techniques. Isolation of the product and subsequent weighing was used most often. When the product was not isolated either an internal standard (chlorobenzene) in the GC/MS was used or a standard titration procedure utilizing HBr/glacial acetic acid was used.[17] Reagent grade chemicals were used when available without further purification, with the exception of the 70%

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[17] Durbetaki, A. J. *Anal. Chem.* **1956**, *28*, 2000.

tert-butyl hydroperoxide/30% water solution which was dried over $MgSO_4$ when mentioned.

Dihydroxylation of Cyclohexene. A solution of cyclohexene (1.0 mL, 9.89 mmol), 70% aqueous solution of *tert*-butyl hydroperoxide (2.76 mL, 19.78 mmol), and $Mo(CO)_6$ (52 mg, 0.198 mmol) was added to the reaction vessel. This corresponds to a 37% fill of the autoclave with organic substrate. The reactor was then sealed, connected to a high-pressure line, and charged to a total internal pressure of 3200 psi with CO_2. The vessel was placed in a tube furnace preheated to 95−100 °C and allowed to react for 3 h. The internal pressure upon heating was determined using a pressure transducer, and the temperature inside the vessel was monitored with an Omega type K thermocouple. The final pressure of the reaction was approximately 8000 psi at 95 °C. After 3 h the reaction vessel was cooled to room temperature, and the CO_2 pressure was released by bubbling through ether. The walls of the autoclave were rinsed with Et_2O to ensure complete recovery of all organic material. Filtration was used to remove inorganic solids prior to GC/MS. The yield of diol was initially determined by a GC/MS internal standard (chlorobenzene) to be 100%. The ether solvent was removed by conventional methods to yield a white crystalline powder. The solid was weighed and determined to be a quantitative yield of *anti*-1,2-cyclohexanediol. The solid was dissolved in $CDCl_3$, and NMR specta were collected. Standards purchased from Aldrich of the *anti*- and *syn*-diols were used to determine the conformation of the product.

Epoxidation of Cyclohexene. A solution of cyclohexene (1.0 mL, 9.89 mmol), 70% aqueous solution of *tert*-butyl hydroperoxide (1.38 mL, 9.89 mmol), and $Mo(CO)_6$ (52 mg, 0.198 mmol) was added to the reaction vessel. This corresponds to a 24% fill of the autoclave with organic substrate. The reactor was then sealed, connected to a high-pressure line, and charged to a total internal pressure of 3200 psi with CO_2. The vessel was placed in a tube furnace preheated to 80−85 °C and allowed to react for 3 h. The internal pressure upon heating was determined using a pressure transducer, and the temperature inside the vessel was monitored with an Omega type K thermocouple. The final pressure of the reaction was approximately 7500 psi at 80 °C. After 3 h the reaction vessel was cooled to room temperature, and the CO_2 pressure was released by bubbling through ether. The walls of the autoclave were rinsed with Et_2O to ensure complete recovery of all organic material. Filtration was used to remove inorganic solids prior to GC/MS. The yield of epoxide was initially determined by a GC/MS internal standard (chlorobenzene) to be 47%. The product was left in ether and titrated with an HBr/glacial acetic acid solution to confirm the yield of epoxide.

Recharging of Cyclohexene Reactions. A solution of cyclohexene (0.25 mL, 2.47 mmol), 70% aqueous solution of *tert*-butyl hydroperoxide (0.345 mL, 2.47 mmol), and $Mo(CO)_6$ (52 mg, 0.198 mmol) was added to the reaction vessel. This corresponds to a 5.9% fill of the autoclave with organic substrate. The reactor was then sealed, connected to a high-pressure line, and charged to a total internal pressure of 3200 psi with CO_2. The vessel was placed in a tube furnace preheated to 80−85 °C and allowed to react for 3 h. The internal pressure upon heating was determined using a pressure transducer, and the temperature inside the vessel was monitored with an Omega type K thermocouple. The final pressure of the reaction was approximately 7500 psi at 80 °C. After 3 h the reaction vessel was cooled to room temperature, and the CO_2 pressure was slowly released to ensure no loss of catalyst or reactants. The autoclave was then opened, and an aliquot was taken for GC/MS analysis. A solution of cyclohexene (0.25 mL, 2.47 mmol) and a 70% aqueous solution of *tert*-butyl hydroperoxide (0.345 mL, 2.47 mmol) were then added to the reaction vessel. This corresponds to a 11.8% fill of the autoclave with organic substrate. The reactor was then sealed, connected to a high-pressure line, and charged to a total internal pressure of 3200 psi with CO_2. The vessel was returned to the tube furnace preheated to 80−85 °C and allowed to react for 3 h. After 3 h the reaction vessel was cooled to room temperature, and the CO_2 pressure was slowly released to ensure no loss of catalyst or reactants. The walls of the autoclave were rinsed with Et_2O to ensure complete recovery of all organic material. Filtration was used to remove inorganic solids prior to GC/MS. The yield of oxidized product was determined by a GC/MS and show no decrease in reactivity between the first and second batch.

Epoxidation of Cyclooctene. A solution of cyclooctene (1.0 mL, 8.16 mmol), 70% aqueous solution of *tert*-butyl hydroperoxide (3.42 mL, 24.5 mmol), and $Mo(CO)_6$ (43 mg, 0.16 mmol) was added to the reaction vessel. This corresponds to a 43% fill of the autoclave with organic substrate. The reactor was then sealed, connected to a high-pressure line, and charged to a total internal pressure of 3200 psi with CO_2. The vessel was placed in a tube furnace preheated to 85−90 °C and allowed to react for 3 h. The internal pressure upon heating was determined using a pressure transducer, and the temperature inside the vessel was monitored with an Omega type K thermocouple. The final pressure of the reaction was approximately 7750 psi at 86 °C. After 3 h the reaction vessel was cooled to room temperature, and the CO_2 pressure was released by bubbling through ether. The walls of the autoclave were rinsed with Et_2O to ensure complete recovery of all organic material. Filtration was used to remove inorganic solids prior to GC/MS. The yield of epoxide was initially determined by a GC/MS internal standard (chlorobenzene) to be 100%. The product was left in ether and titrated with an HBr/glacial acetic acid solution to confirm the yield of epoxide

Epoxidation of *cis*-2-Heptene. A solution of cyclohexene (1.0 mL, 7.22 mmol), a 5.0−6.0 M solution of *tert*-butyl hydroperoxide in decane (2.31 mL, 21.66 mmol), and $Mo(CO)_6$ (38 mg, 0.144 mmol) was added to the reaction vessel. This corresponds to a 33% fill of the autoclave with organic substrate. The reactor was then sealed, connected to a high-pressure line, and charged to a total internal pressure of 3200 psi with CO_2. The vessel was placed in a tube furnace preheated to 90−95 °C and allowed to react for 3 h. The internal pressure upon heating was determined using a pressure transducer, and the temperature inside the vessel was monitored with an Omega type K thermocouple. The final pressure of the reaction was approximately 8500 psi at 95 °C. After 3 h the reaction vessel was cooled to room temperature, and the CO_2 pressure was released by bubbling through ether. The walls of the autoclave were rinsed with Et_2O to ensure complete recovery of all organic material. Filtration was used to remove inorganic solids prior to GC/MS. The yield of epoxide was initially determined by a GC/MS internal standard (chlorobenzene) to be 23%. The product was left in ether and titrated with an HBr/glacial acetic acid solution to confirm the yield of epoxide.

Synthesis of $Mo(CO)_5(C_8H_{14})$. $Mo(CO)_6$ (3.75 g, 14.2 mmol) and *cis*-cyclooctene (25 mL, 192 mmol) were added to a 1 L UV immersion well. Approximately 750 mL of hexane was added, and the solution was then degassed with N_2. The well was equipped with a constant flow of N_2 and a bubbler to allow for the escape of CO and N_2. The reaction was stirred and irradiated with a mercury UV lamp for 20 h. The straw colored solution was then transferred via cannula to a 1 L flask where the volume was reduced to half under vacuum. The reaction was then cooled to −78 °C and allowed to sit for 3 h to allow for the crystallization of the product. The mother liquor was decanted, and the straw colored solid was pumped to dryness at −78 °C. The product was stored under nitrogen in a freezer until it was loaded into the autoclave.

Epoxidation of Cyclohexene with $Mo(CO)_5(C_8H_{14})$. A solution of cyclohexene (1.0 mL, 9.89 mmol), 70% aqueous solution of *tert*-butyl hydroperoxide (1.38 mL, 9.89 mmol), and $Mo(CO)_5(C_8H_{14})$ (52 mg, 0.198 mmol) was added to the reaction vessel. This corresponds to a 24% fill of the autoclave with organic substrate. The reactor was then sealed, connected to a high-pressure line, and charged to a total internal pressure of 3200 psi with CO_2. The vessel was placed in a tube furnace preheated to 68 °C and allowed to react for 90 min. The internal pressure upon heating was determined using a pressure transducer, and the temperature inside the vessel was monitored with an Omega type K thermocouple. The final pressure of the reaction was approximately 6500 psi at 68 °C. After 90 min the reaction vessel was cooled to room temperature, and the CO_2 pressure was released by bubbling through ether. The walls of the autoclave were rinsed with Et_2O to ensure complete recovery of all organic material. Filtration was used to remove inorganic solids prior to GC/MS. The yield of epoxide was initially determined by a GC/MS internal standard (chlorobenzene) to be 50%.

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