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The Diastereoselective Epoxidation of Olefins in Supercritical Carbon Dioxide.

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Abstract: Allylic alcohols are epoxidized with tert-butyl hydroperoxide in the presence of a vanadyl salen oxo-transfer catalyst in supercritical CO_2. The metal catalyst was prepared in a simple two step, Schiff base reaction to form the salen ligand, followed by complexation to the vanadyl group. The epoxidation reactions are clean and give both high yields and good diastereoselectivity.

Supercritical (SC) CO_2 (critical point: 72.8atm, 31 °C) is rapidly emerging as an alternative solvent for various chemical transformations because it is non-toxic and environmentally benign.[1] The epoxidation of olefins in the presence of a terminal oxygen source and a transition metal oxo-transfer catalyst have traditionally been performed in toxic solvents such as methylene chloride.[2] The synthesis of epoxides with asymmetric Mn^{III}(salen)Cl salts has provided a powerful means of enantioselective epoxidation,[3] because of its ability to produce two stereocenters in one reaction. The catalyst is also attractive because of the simplicity in its synthesis.[3,4] However, one of the problems encountered with SC CO_2 is the inability to dissolve many of the commonly used terminal oxygen sources employed in Mn^{III} catalyzed epoxidations (e.g. NaOCl, iodosylbenzene). Alkylhydroperoxides are soluble in SC CO_2, and we recently achieved success with many simple symmetric catalysts.[5] However these soluble hydroperoxides homolytically decompose in the presence of Mn^{III} salts,[6] leading to undesired products (e.g. dialkylperoxides, allylic alcohols, allylic ketones), and little of the desired epoxide.

Previous success with the $VO(acac)_2$/t-BuOOH catalyst system in SC CO_2[7] suggested the possibility of designing a novel vanadium(IV) catalyst with a salen backbone, having the reactivity of $VO(acac)_2$ and selectivity of the Mn^{III}(salen). The addition of 1 equiv. of the crystalline salen derivative (salen*) to a solution of $VO(acac)_2$ (1 equiv.) in CH_2Cl_2 immediately gave a dark green solution. Stirring for three hours at room temperature, followed by removal of the solvent yielded

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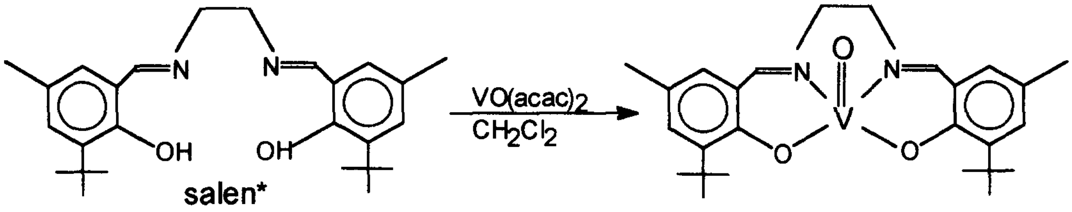
the crude hunter green product in powder form. This crude powder was dissolved in CH_2Cl_2, layered with petroleum ether (4 equiv.), and allowed to recrystallize in a freezer overnight (-3 °C). The product was filtered and the recrystallization process was repeated three times (yield 63%). Absorption bands at 980 cm^{-1} and 1200 cm^{-1} were observed in the IR which correspond to the V=O and the C=N stretching respectively. Further characterization was gained by direct insertion mass spectrometry (MWT=473), single crystal X-ray diffraction,[8] and elemental analysis (Calc:C=65.9%, H=7.2%, N=5.9%; Found C=65.9%, H=7.2%, N=5.9%).



The epoxidation of a range of allylic alcohols using the $V^{IV}O$(salen*)/t-BuOOH system in SC CO_2 was examined. In a typical procedure, 70% aqueous t-BuOOH (5.77mmol, 1.0mL) and geraniol (5.77mmol, 0.81mL) are added to a 316 SS high pressure autoclave with a 10 mL total volume. The catalyst, (0.0577mmol, 27 mg) is subsequently loaded into a small, open ended pyrex tube, and inserted open end up in the reaction vessel. (It is necessary to separate the metal catalyst and oxygen source until the solvent CO_2 can be added.) The reaction vessel is sealed, charged with an initial pressure of 3200 psi CO_2, and placed in a pre-heated, shaking water bath for 1 day. After 24 hours of heating and shaking, the reaction vessel is cooled to room temperature, the CO_2 vented, and the crude product analyzed for yield and selectivity by conventional methods (G. C. analysis, ^1H and ^{13}C NMR, isolation of pure product by chromatography). In order to ensure that the reactions are homogeneous, a series of experiments were performed in a reaction vessel containing quartz windows at each end. From visual observations it was confirmed that the substrate and catalyst are miscible in the CO_2, as only one phase is observed after shaking in the waterbath at 40 °C. It should be noted that the catalyst can be recovered and reused with similar activity, providing a minimal turnover number of 150.

$V^{IV}O$(salen*)/t-BuOOH in SC CO_2 showed epoxidation reactivity similar to many traditional oxygen transfer catalysts in CH_2Cl_2. The rates of reaction appeared to be slightly slower in the CO_2 solvent, although most reactions were nearly complete after 24 hours. Entries 1-3 demonstrate that this catalyst shows good diastereoselectivity for the erythro epoxide, as determined by NMR. The reactions proceed in high yields for a wide variety of allylic alcohols, but olefins without alcohols are epoxidized sluggishly in yields less than 30%. The high diastereoselectivity of this reaction

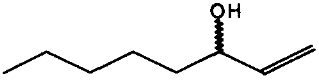
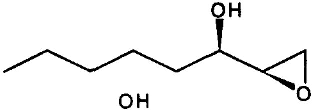
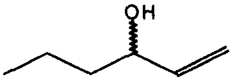
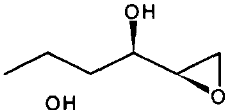
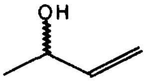
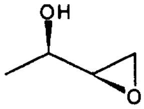
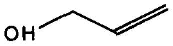
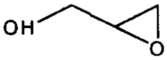
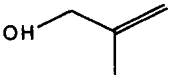
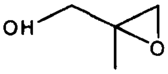
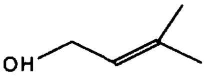
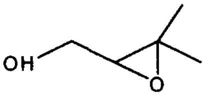
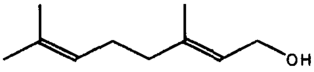
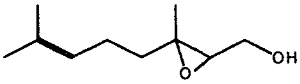
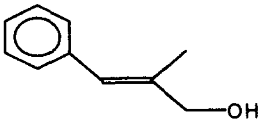
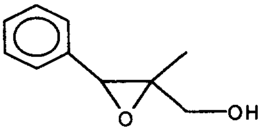
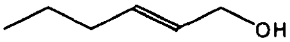
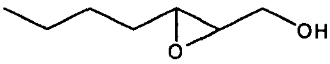
Entry	Olefin^a	temp/time	epoxide	%yield/%de
1		50°C/48h		64%/70%erythro
2		45°C/48h		47%/72%erythro
3		50°C/48h		76%/69%erythro
4		45°C/48h		40%(>95%)
5		45°C/48h		50%(75%)
6		45°C/24h		40%(88%)
7		45°C/48h		99%(>99%)
8		45°C/48h		86%(90%)
9		45°C/24h		57%(87%)
10		45°C/48h		36%(83%)
11		40°C/72h		33%(60%)

Table: A 1:1 ratio of olefin to 70% aq. t-BuOOH (Aldrich) was used for all reactions in 3200 psi SC CO_2. The selectivity for epoxide is given in parentheses.

compared to unsubstituted olefins, coupled with the increased rates of epoxidation for the allylic alcohols suggest coordination of the alcohol substrate to the metal center prior to oxygen transfer. The reactions are very clean and give a high yield of epoxide with only minor side products. Further oxidation of the allylic alcohol to the allylic ketone is observed in nearly every reaction, but the yield of enone is never more than 10%. Reaction in the absence of catalyst gives no epoxidation.

In conclusion, we have shown that SC CO_2 is a viable solvent for the clean, selective epoxidation of a wide array of allylic alcohols. Using the new VO^{IV}(salen*) epoxidation catalyst, the yields and diastereoselectivities are all comparable to those obtained in traditional environmentally hazardous solvents. More research is being conducted to investigate the possibility of building an asymmetric ligand for enantioselective synthesis.

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