

## Olefin Epoxidations Using the Dicyclohexylcarbodiimide–H<sub>2</sub>O<sub>2</sub> System

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### Introduction

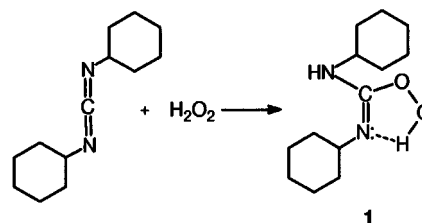
As part of our continuing interest in oxidizing systems which can transfer O atoms to organic and biological substrates, we have been studying the system consisting of a carbodiimide and H<sub>2</sub>O<sub>2</sub>. A number of reports have described the use of such systems for accomplishing the desired O atom transfer with varying degrees of success. Hamilton and co-workers<sup>1</sup> have shown that a system consisting of an arene, an aliphatic carbodiimide, H<sub>2</sub>O<sub>2</sub>, and an acid leads to arene oxide formation in ca. 30% yield. Subsequently Rebek et al. reported<sup>2</sup> that the commercially available dicyclohexylcarbodiimide failed to epoxidize cyclododecenes in THF containing H<sub>2</sub>O<sub>2</sub>. On the other hand, use of the carbodiimide, *N*-benzoyl-*N*-*tert*-butylcarbodiimide, and H<sub>2</sub>O<sub>2</sub> led to epoxidation of a number of olefins in good yields.<sup>2</sup> More recently the dicyclohexylcarbodiimide/aqueous H<sub>2</sub>O<sub>2</sub> system has been shown to give styrene oxide in 75% yield.<sup>3</sup> In the work reported here we have reexamined the use of the carbodiimide/H<sub>2</sub>O<sub>2</sub> system under conditions where the H<sub>2</sub>O<sub>2</sub> is delivered as the urea–H<sub>2</sub>O<sub>2</sub> (UHP) complex. These conditions give excellent yields of epoxides in a range of unsaturated substrates. UHP provides a number of advantages as a source of H<sub>2</sub>O<sub>2</sub>.<sup>4</sup> It is a solid which is easier to use and transport, and it may be used in nonprotic solvents.

### Results and Discussion

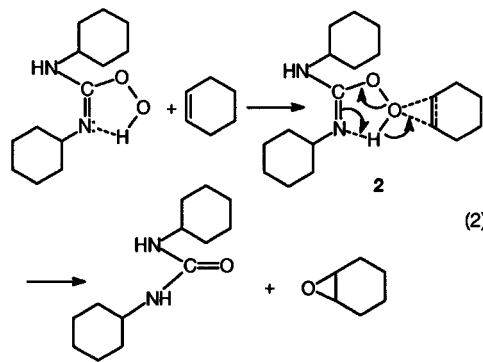
We have oxidized a variety of olefins using UHP as a source of H<sub>2</sub>O<sub>2</sub>. In the general procedure the olefin, dicyclohexylcarbodiimide (DCC), UHP, and potassium bicarbonate are combined together in methanol or ethanol as solvent. Earlier experience<sup>5</sup> using this system for epoxidizing models for lignin indicated that epoxidation yields are higher when basic rather than acidic or neutral reaction conditions are used. The reactions were run at room temperature usually for 4 h. In the case of

cyclohexene, a 7 h reaction time was used. Also, in the cyclohexene case we have shown that no epoxidation occurs under the reaction conditions when DCC is not present. When methanol is the solvent, the yields are generally high (Table 1). The exceptions are those unsaturated substrates containing electron-withdrawing substituents (entries 7 and 8). When ethanol is the solvent, the yields are uniformly lower (23–80%). The conditions used here are also able to convert cyclododecene (cis and trans mixture) to the stereoisomeric epoxides in 70% yield when methanol is the solvent (entry 10). This contrasts with the earlier report<sup>2</sup> indicating that the use of DCC with H<sub>2</sub>O<sub>2</sub> in THF failed to give epoxidation with cyclododecene.

The reaction presumably occurs via an adduct (**1**) between DCC and H<sub>2</sub>O<sub>2</sub> (eq 1). Intramolecular H-



bonding in adduct **1** is probably necessary for the epoxidation to occur in a manner similar to that shown in peracids.<sup>2,6</sup> In peracids, epoxidation rates decrease as the Lewis basicity of the solvent increases. This is interpreted<sup>2,6</sup> as indicating that the increased basicity of the solvent leads to greater disruption of the intramolecular H-bond in the peracid. A similar solvent influence on **1** may explain the observed yield differences between methanol and ethanol solvents in the current work. We postulate that O transfer from **1** occurs in a manner analogous to that in peracids. The process is illustrated in eq 2 using cyclohexene as substrate. Collapse of the



transition state **2** in the manner shown leads to the urea and epoxide products.

### Experimental Section

**Materials.** Urea hydrogen peroxide (UHP), cyclohexene, 1-methyl-1-cyclohexene,  $\alpha$ -ionone,  $\alpha$ -methylstyrene, norbornylene, *trans*- $\beta$ -methyl- $\beta$ -nitrostyrene, and ethyl *trans*-cinnamate were all obtained from Aldrich. *trans*- $\beta$ -Methylstyrene (Wiley),

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**Table 1. Epoxidation of Olefins Using the Dicyclohexylcarbodiimide/UHP System<sup>a</sup>**

Entry	Substrate	Solvent mL	Time h	Temp °C	Product	% Yield
1		CH <sub>3</sub> OH	4	RT		96
2		CH <sub>3</sub> OH	4	RT		81
3		CH <sub>3</sub> OH	4	RT		84
4		CH <sub>3</sub> OH	4	RT		94
5 <sup>b</sup>		CH <sub>3</sub> OH	4	RT		95
6		CH <sub>3</sub> OH	4	RT		75
7		CH <sub>3</sub> OH	4	RT		19(45) <sup>c</sup>
8		CH <sub>3</sub> OH	4	RT		40(10) <sup>d</sup>
9		CH <sub>3</sub> OH	4	RT		90
10		CH <sub>3</sub> OH	4	RT		73

<sup>a</sup> Reactants in a molecular ratio of olefin/DCC/UHP (1:2:12); yields are GLC yields. <sup>b</sup> No reaction without DCC. <sup>c</sup> Yield in parentheses denotes the transesterified product with methanol. <sup>d</sup> Yields in the parentheses denote the side chain epoxidation product.

styrene (Matheson, Coleman, and Bell), and dicyclohexylcarbodiimide (DCC) (Mallinckrodt) were all used as received. Potassium bicarbonate was purchased from Mallinckrodt. Cyclododecene [Aldrich, mixture of cis and trans (65%)] was used as such. Methanol (Fisher reagent grade) was fractionally distilled over magnesium methoxide. Hexane, ethyl acetate, diethyl ether, and methylene chloride (all from Fisher) were distilled prior to use.

**Instrumentation.** <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on a 300 MHz NMR spectrometer with tetramethylsilane as internal standard and CDCl<sub>3</sub> as solvent. Electron impact (EI) mass spectra were recorded at 70 eV ionizing voltage on an EI quadrupole mass spectrometer interfaced with a gas chromatograph fitted with a 12 m × 0.2 mm × 0.33 μm Ultra-1 (cross-linked methyl silicone) column. Chromatographic separations on the Chromatotron were accomplished using 2 mm Kieselgel 60 PF 254 plates. Gas chromatography was performed on a capillary gas chromatograph using a flame ionization detector, a fused silica DB-5 capillary column (30 m × 0.318 mm, film thickness 0.5 μm), and He as the carrier gas.

**General Procedure for the Epoxidations.** The olefin (1 mmol), DCC (0.412 g, 2 mmol), UHP (1.12 g, 12 mmol), and KHCO<sub>3</sub> (0.2 g, 2 mmol) were placed in a 25 mL round-bottom flask and methanol or ethanol (5 mL) added. The reaction mixture was stirred at room temperature for 4 or 7 h. Water (10 mL) was then added to the reaction mixture and the mixture extracted with either diethyl ether or dichloromethane (30 mL). The extract was dried over anhydrous sodium sulfate. The products were isolated by chromatography using hexane (80–90%) and diethyl ether (10–20%) as eluent and characterized by NMR and mass spectroscopy. Yields were determined by quantitative GLC using the internal standard method. All the

epoxides in Table 1 were prepared following this procedure. A sample is given here.

**trans-β-Methyl-β-nitrostyrene Oxide.** The general procedure was followed to give a residue which was chromatographed to give a colorless liquid. The product was identified by comparing its NMR spectrum with that in the literature<sup>7</sup> and on the basis of the following data: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.83 (s, 3H), 4.57 (s, 1H), 7.32–7.48 (m, 5H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 12.78, 62.91, 89.11, 126.55, 128.92, 129.58, 131.1. Mass spectrum (EI, 70 eV): 179 (M<sup>+</sup>, 0.26), 105 (base peak), calcd for C<sub>9</sub>H<sub>9</sub>NO<sub>3</sub> 179.17.

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**Supporting Information Available:** <sup>13</sup>C and <sup>1</sup>H NMR and mass spectral data for the product epoxides shown in Table 1 (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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