A New and Efficient Method for the Selective Olefination of Aldehydes with Ethyl Diazoacetate Catalyzed by an Iron(II) Porphyrin Complex

Gholam A. Mirafzal
Iowa State University

Guilong Cheng
Iowa State University

L. Keith Woo
Iowa State University, kwoo@iastate.edu
Transition metal complexes based on porphyrins and on a variety of ancillary ligands have been used extensively by this group and others to catalyze the cyclopropanation of alkenes with ethyl diazoacetate and other suitable diazo reagents. In this communication, we describe a novel extension of the catalytic activity of metallocorphyrins with the first use of an iron(II) porphyrin complex as a catalyst for the efficient and selective olefination of aldehydes. The generation of a carbon—carbon double bond is one of the important synthetic transformations in organic chemistry, especially in the areas of natural products and polymer synthesis. Although other metal complexes can catalyze this reaction, the iron system is especially proficient and cost-effective.

Olefination of aromatic and aliphatic aldehydes (Table 1) was achieved in excellent yield at ambient temperature using 2 equiv of ethyl diazoacetate, N\textsubscript{2}CHCO\textsubscript{2}Et (EDA), and 1.1 equiv of triphenylphosphine, Ph\textsubscript{3}P, in the presence of catalytic amounts of iron(II) meso-tetrapropylporphyrin, Fe\textsubscript{II}(TTP) (1 — 2 mol %), in toluene (eq 1). Ratios of reagents were selected for convenient reaction times, high yields, and ease of purification. Ethyl maleate and furmate were also observed as side products, but were readily removed by chromatography. Treatment of benzaldehyde, 1, with EDA/Ph\textsubscript{3}P/Fe\textsubscript{II}(TTP) in toluene at ambient temperature resulted in 98% conversion to ethyl cinnamate after a reaction time of 2 days. GC and 1 H NMR analysis confirmed a high selectivity for the \( \text{cis} \) isomer appeared at a shorter retention time versus the \( \text{trans} \) isomer. The progress of reaction was monitored by GC. Isolated yield, 1 H NMR analysis showed a \( J_{\text{HH}} \) of 12.6 Hz for \text{cis}-hydrogens and a \( J_{\text{HH}} \) of 15.9 Hz for \text{trans}-hydrogens and a

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\text{RCO} + \text{N}_{2}\text{CHCO}_{2}\text{Et} + \text{PhP} \xrightarrow{\text{Fe}^{\text{II}}(\text{TTP})} \text{RCH=CHCO}_{2}\text{Et} + \text{PhP}=\text{O} \quad \text{(1)}
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R = Ph, \( p-\text{CH}_{2}\text{C}_{6}\text{H}_{4}, \) \( p-\text{NO}_{2}\text{C}_{6}\text{H}_{4}, \) \( p-\text{Cl}_{2}\text{C}_{6}\text{H}_{4}, \) PhCH\textsubscript{2}-, (Ph)\textsubscript{2}CH-.

Preliminary studies were undertaken to probe the mechanism for this olefination process. A catalytic cycle (Scheme 1) proposed for the analogous methyltrioxorhenium (MTO) catalyzed reaction involves oxygen atom abstraction from MTO by phosphate. The resultant Re(V) dioxo complex reacts with a diazo reagent to produce a carbene complex that subsequently forms a metalla-oxetane species in the presence of aldehydes. Fragmentation of the metalla-oxetane produces the new olefin and regenerates MTO. We presume that the active species in the iron porphyrin catalyzed reactions is an iron—carbene complex formed by reaction of the iron(II) porphyrin with EDA. Related complexes prepared from mesityl diazomethane and trimethylsilyl diazomethane are readily observed by 1 H NMR spectroscopy. However, (TTP)Fe=CHCO\textsubscript{2}Et is too reactive to isolate or detect spectroscopically. The more electron rich osmium analogue, (TTP)Os=CHCO\textsubscript{2}Et, has been isolated and is well characterized. If a metalla-oxetane intermediate is involved, the iron—carbene complex may serve as a nucleophile that attacks the carbonyl functional group of aldehydes. This is consistent with the higher reactivity of electron poor aldehydes (vide infra). Subsequent ring opening of the metalla-oxetane would produce an olefin and an o xoiron porphyrin complex. Regeneration of Fe(TTP) would occur by oxidation of phosphate to phosphine oxide.

For this mechanism to be viable, the inner sphere reaction between unencumbered oxoiron(IV) and iron(II) porphyrins, producing a \( \mu \)-oxo Fe(III) dimer, must be minimal. Formation of the Fe(III) dimer would serve to quickly inactivate the catalyst. However, rapid deactivation was not observed and attempts were made to test for the presence of the iron(IV) oxo complex with other oxygen atom acceptors. Olefins were chosen since oxoiron(IV) porphyrin complexes effectively epoxidize the double bond. When an Fe(TTP)-catalyzed reaction of benzaldehyde and EDA was run
with styrene substituted as the reductant in place of Ph₃P, no ethyl cinnaamate was observed. The only product was ethyl 2-phenyl-cyclopropylcarboxylate (100%), indicating that styrene was much more efficient in reacting with the carbene complex than was the aldehyde. An alternative oxygen atom acceptor, cyclohexene, was subsequently employed. I,2-Substituted olefins are poor cyclopropanation substrates,14 but readily undergo epoxidation.9 However, using cyclohexene in place of Ph₃P under catalytic conditions resulted in neither olefination of the aldehyde nor epoxidation of the alkene. The organic products were ethyl maleate and fumarate produced by carbene dimerization. These studies indicated that an iron–carbene complex was involved but that the oxoiron(V) species was an unlikely candidate.

The reactivity profile of the Fe(TTP)-catalyzed olefination reaction differs significantly from the MoO₅(S₂CN(CH₂)₂)-mediated process.16 The catalytic cycle for the Mo system purportedly involves metalloazines, 10 (Et₂NCS)₂OMoO₂PPh₃, and phosphines, Ph₃P=N=N=CH₂OEt₄. The phosphine is presumably responsible for the formation of large amounts of azines with electron-poor aldehydes in this system.

On the basis of the above data, the most likely mechanism for the Fe(TTP) olefination reaction is shown in Scheme 2. In this process, the Fe complex serves to catalytically convert the diene reagent and phosphine to phosphorane. The phosphorane in turn produces the alkene. The organic products were ethyl maleate and fumarate resulting in neither olefination of the aldehyde nor epoxidation of the alkene. The organic products were ethyl maleate and fumarate produced by carbene dimerization. These studies indicated that an iron–carbene complex was involved but that the oxoiron(V) species was an unlikely candidate.

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