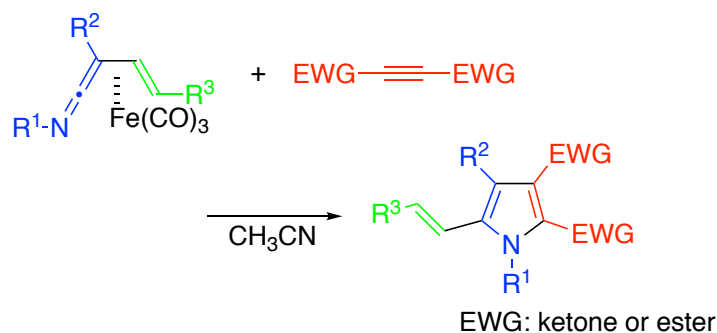


Pyrrole Formation via Reactivity of η^4 -(Vinylketenimine)iron Complexes with Electron-Deficient Alkynes

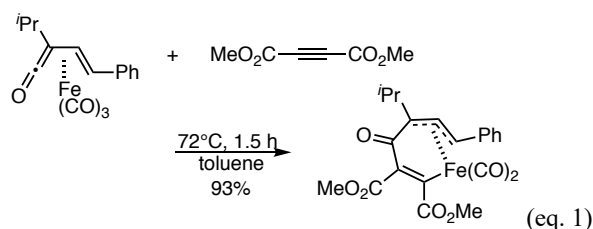
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ABSTRACT: When electron-deficient alkynes reacted with η^4 -(vinylketenimine)iron complexes, pyrroles were produced. Pyrrole formation involved the [2+3] cycloaddition of alkyne to the ketenimine moiety, migration of the vinyl group, and decomplexation. Either alkynes bearing two electron-withdrawing groups, or terminal alkynes with an electron-withdrawing group reacted to generate pyrroles.

η^4 -(1,3-Diene)iron complexes are common in organometallic chemistry, and particularly in organic synthesis,^{1,2} owing to their high availability, thermal stability, and low toxicity. As part of our continuing interest in the chemistry of the organoiron compounds,³ we recently reported that treatment of η^4 -(1,3-diene)iron complexes with Lewis acid in the presence of an aromatic compound under a carbon monoxide (CO) atmosphere produced η^4 -(vinylketene)iron complexes.⁴ Additionally, the iron complexes of vinylketenes exhibit noteworthy synthetic transformations.^{5,6} For example, electron-deficient alkynes add to the vinylketene complexes via insertion to yield stable 1:1 adducts (eq. 1).⁷ However, the particulars of the reactivity of η^4 -(vinylketenimine)iron complexes,^{8,9} which are easily prepared from the corresponding (vinylketene)iron complexes,¹⁰ are largely unknown. Based on η^4 -(vinylketene)iron complexes reactivity (eq. 1), we envisaged that (vinylketenimine)iron complexes could be converted into η^3 -allyl iron complexes through alkyne insertion. In the current study, we explored the potential for this reactivity and found that pyrroles were formed when (vinylketenimine)iron complexes were treated with electron-deficient alkynes.



(Vinylketenimine)iron complex **1a** was prepared from a η^4 -(vinylketene)iron complex⁴ and diethyl *N*-octylphosphoramidate, and subsequently treated with diethyl acetylenedicarboxylate (2.0 equiv.) in toluene (eq.2), to yield a yellow oil. Infrared and NMR spectral analysis indicated that this oil lacked the carbonyl absorptions of the expected iron complex **3a**, but instead contained two ethoxycarbonyl groups **2a**. Hydrolysis of the yellow oil yielded crystalline dicarboxylic acid **4a** and the structure of **2a** was established by single-crystal X-ray analysis of **4a**. The molecular structure of **4a** is depicted in Figure 1. The treatment of a vinylketenimine with dimethyl acetylenedicarboxylate is known to give 3-aminophthalic acid dimethyl ester via [4+2] cycloaddition.¹¹ In our case, the [4+2] cycloaddition was suppressed by the coordination of an iron carbonyl, and a nitrogen atom of the imine added an alkyne carbon, giving a pyrrole ring. This pyrrole formation was only achieved with the involvement of an iron atom.

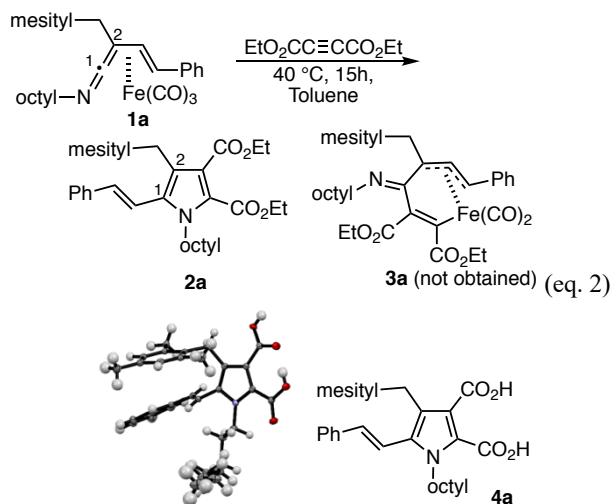
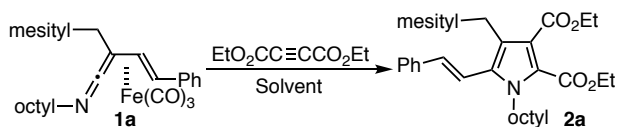


Figure 1. An ORTEP diagram of the crystal structure of **4a** (50% probability)

This is the first documented observation of a pyrrole formation using a η^4 -(vinylketenimine)iron complex. The reaction involved the [2+3] cycloaddition of alkyne to the ketenimine moiety ($\text{N}=\text{C}(1)=\text{C}(2)$), the migration of the styryl group (from C(2) to C(1)), and the decomplexation. This novel pyrrole formation via reaction of **1a** with diethyl acetylenedicarboxylate was optimized through utilization of different solvents (Table 1). All solvents examined generated the corresponding pyrrole **2a** in good yield, with CH_3CN the most effective.

Table 1 Product yield from the reaction of 1a and diethyl acetylenedicarboxylate under different solvent conditions.^a



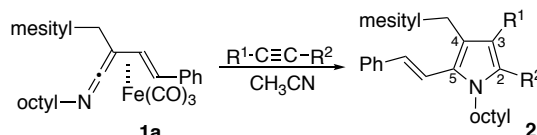
| run | Solvent | Time (h) | Yield ^b (%) |
|-----|--------------------------|----------|------------------------|
| 1 | Toluene | 15 | 63 |
| 2 | CH_2Cl_2 | 5 | 75 |
| 3 | CH_3CN | 0.5 | 87 |
| 4 | THF | 3 | 70 |
| 5 | DMF | 1.5 | 72 |

^a Reaction conditions: **1a** (1.0 equiv.), diethyl acetylenedicarboxylate (2.0 equiv.), at 40 °C under N_2 . The reaction was stirred until complete consumption of the starting material **1a**. ^b Isolated yield based on **1a**.

We then examined the reaction of several alkynes with the iron complex **1a** and the results are summarized in Table 2. Pyrroles were generated when either alkynes two strong electron-withdrawing groups (runs 1 and 4), or terminal alkynes with an electron-withdrawing group (runs 2 and 5), were used. However, reactions in which alkynes contained an electron-donating group (runs 3, 6–9) did not proceed, resulting in decomposition of **1a**. The regiochemistry of the products from runs 2 and 5 (Table 2) has been confirmed by two-dimensional (2D) NOE spectroscopy (NOESY). A cross-peak was observed between the aromatic proton of the pyrrole ring, and the methylene protons attached to pyrrole nitrogen, but not

between the aromatic proton, and the benzylic methylene protons. The observed cross-peak is consistent with a structure containing a 2-unsubstituted pyrrole (Figure 2). Collectively, these results indicate that the reaction probably proceeds *via* a nucleophilic attack of the ketenimine nitrogen atom on the beta carbon of an α,β -unsaturated carbonyl compound.

Table 2 Reaction between the η^4 -(vinylketenimine)iron complex 1a and alkynes^a



| run | R ¹ | R ² | Conditions | Product | Yield (%) ^b |
|-----|------------------------|-----------------|--------------|-----------|------------------------|
| 1 | EtOCO | EtOCO | 40 °C, 0.5 h | 2a | 87 |
| 2 | EtOCO | H | 40 °C, 3.5 h | 2b | 80 |
| 3 | EtOCO | ⁿ Bu | reflux, 12 h | – | – |
| 4 | PhCO | PhCO | 40 °C, 3 h | 2c | 75 |
| 5 | PhCO | H | 40 °C, 3 h | 2d | 87 |
| 6 | PhCO | ⁿ Bu | reflux, 12 h | – | – |
| 7 | Ph | H | reflux, 12 h | – | – |
| 8 | Hexyl | H | reflux, 12 h | – | – |
| 9 | Me_3Si | H | reflux, 12 h | – | – |

^a Reaction conditions: **1a** (1.0 equiv.), alkyne (2.0 equiv.) under N_2 . ^b Isolated yield based on **1a**.

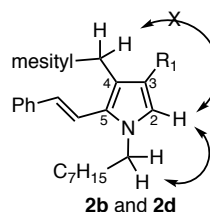
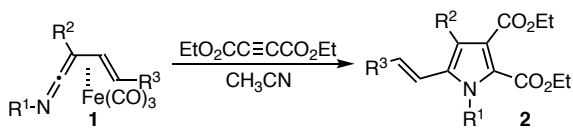


Figure 2. Two dimensional NOE spectroscopy (NOESY) correlation of **2b** and **2d**.

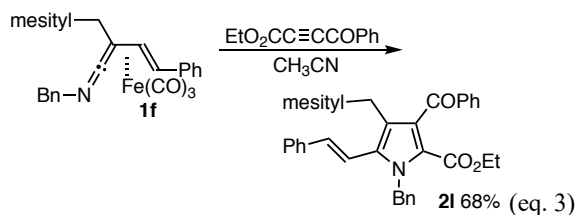
Next, η^4 -(vinylketenimine)iron complexes were treated with diethyl acetylenedicarboxylate to generate pyrroles (Table 3). The pyrrole formation was compatible with a variety of vinylketenimine complexes. The iron complex with a Ph or isopropyl group as R² underwent the pyrrole formation at a lower temperature than the complex with a bulky mesityl-CH₂ group (runs 1 and 2). A higher reaction temperature was required for the sterically hindered, less nucleophilic *N*-cyclohexyl or *N*-phenyl ketenimine complexes (runs 6 and 7). Iron complex **1f** was subjected to treatment with an unsymmetrical alkyne bearing both ester and ketone groups (two different electron-withdrawing groups; eq. 3), which generated predominantly the expected pyrrole product, which possessed a greater electron-withdrawing group at C3 (**2i**). The structure of **2i** was confirmed by X-ray analysis (see Supporting Information), and demonstrated that the reaction involved the nucleophilic attack of the ketenimine nitrogen on the more electron-deficient β carbon of the α,β -unsaturated ketone rather than that of the ester. This result is supported by the observed selectivity of the reaction between **1a** and terminal alkynes above.

Table 3 Reaction of η^4 -(vinylketenimine)iron complexes **1** with diethyl acetylenedicarboxylate^a



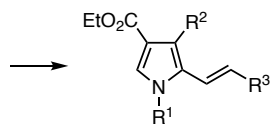
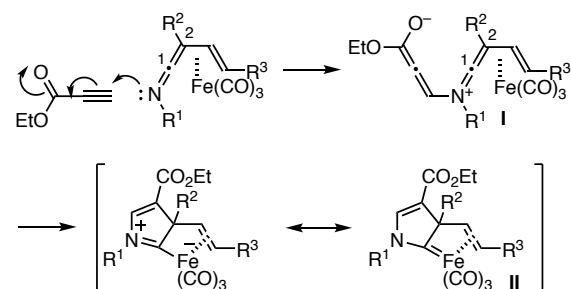
| run | 1 | R ¹ | R ² | R ³ | Conditions | Product | Yield (%) ^b |
|-----|-----------|----------------|-------------------------|----------------|-------------|-----------|------------------------|
| 1 | 1b | octyl | isopropyl | Ph | rt, 6 h | 2e | 75 |
| 2 | 1c | octyl | Ph | Ph | rt, 1 h | 2f | 62 |
| 3 | 1d | allyl | mesityl-CH ₂ | Ph | 40°C, 0.5 h | 2g | 69 |
| 4 | 1e | allyl | mesityl-CH ₂ | H | 40°C, 3 h | 2h | 61 |
| 5 | 1f | benzyl | mesityl-CH ₂ | Ph | 40°C, 3.5 h | 2i | 71 |
| 6 | 1g | cyclohexyl | mesityl-CH ₂ | Ph | 60°C, 3 h | 2j | 82 |
| 7 | 1h | Ph | mesityl-CH ₂ | Ph | 60°C, 6 h | 2k | 59 |

^a Reaction conditions: **1** (1.0 equiv.), acetylenedicarboxylate (2.0 equiv.) under N₂. ^b Isolated yield based on **1**.



We have proposed the following mechanism for the observed pyrrole formation (Scheme 1). Addition of η^4 -(vinylketenimine)iron complex to ethyl propiolate resulted in formation of an enolate intermediate **I**, stimulated by the nucleophilic nitrogen atom of the ketenimine.⁹ Subsequent intramolecular addition of enolate to the keteniminium moiety occurred at C-2⁸ to yield a η^3 -vinylcarbene intermediate **II**.^{9,12,13} Complex **II** then underwent a dominant 1,2-styryl group migration,^{14,15} which suppressed the 1,2-migration of the alkyl group (R²) probably due to the coordination of a styryl double bond to iron.

Scheme 1. Proposed reaction mechanism for pyrrole formation from a η^4 -(vinylketenimine)iron complex



In conclusion, this study documents organic transformation of η^4 -(vinylketenimine)iron complexes for the first time. The treatment of η^4 -(vinylketenimine)iron complexes with electron-deficient alkynes yielded polysubstituted pyrroles. This reaction began with a nucleophilic attack of the ketenimine nitrogen atom on the alkyne, and proceeded via a η^3 -vinylcarbene iron complex intermediate. Future experiments will focus on detailing the reactivity of the η^4 -(vinylketenimine)iron complexes and developing the reaction using electron-deficient alkenes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Experimental details; ¹H NMR and ¹³C NMR spectra; X-ray crystallographic data for **4a** and **2i** (PDF)

ACCESSION CODES

CCDC 2074661 (**4a**) and 2074664 (**2i**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

We gratefully acknowledge Grant-in-Aid for Scientific Research from MEXT for financial support. We also thank the Center for Instrumental Analysis KIT for analytical data measurement.

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(15) A reviewer suggested that 1,2-styryl shift involves an oxidative addition and a reductive elimination via an allyl-iron formation;

we think that it is possible and thank the reviewer for this suggestion.

