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Ferric(III) Nitrate: An Efficient Catalyst for the Regioselective Friedel–Crafts Reactions of Indoles and *tert*-Enamides in Water

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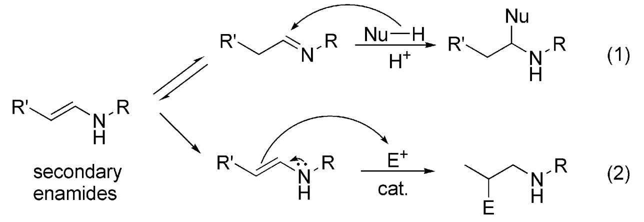
Keywords: Iron / Alkylation / Nitrogen heterocycles / Water chemistry / Green chemistry

The ferric nitrate catalyzed Friedel–Crafts reactions of various indoles and tertiary enamides, which proceed in water at room temperature, are demonstrated for an efficient, atom-economical and environmentally friendly route to produce indole derivatives under mild conditions. Based on experimental data and mechanistic studies, the iron(III) ion was found to activate the electron-rich C=C bond with collaboration of the carbonyl group in the catalytic process.

Introduction

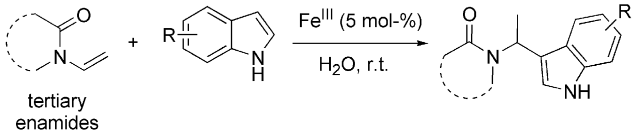
Indole, as a basic backbone, is frequently found in many natural bioactive products, marketed drugs, functional materials, and agrochemicals.[1] Much attention has been paid to its synthesis and modification in the past several decades. The Friedel–Crafts (F–C) alkylation reaction of indole was one of the most powerful routes to synthesize indole derivatives.[2] Among the various alkylation reagents (e.g., alcohols,[3] esters,[4] and olefins[5]), olefins are highly attractive, as they undergo atom-economical processes. Great progress has been made in the F–C alkylation of indole with electron-deficient olefins. However, the applications of electron-rich olefins in such a reaction still remain a challenge.

Enamide, as a good candidate in the family of electron-rich olefins, has been widely used in organic reactions.[6] Although much less attention has been focused on the electrophilicity of enamides than its nucleophilicity, recent examples have revealed successfully on its electrophilic role (Scheme 1).[7] The groups of Terada and Zhou reported the enantioselective F–C reactions of indoles and enamides, respectively, in which enamides had to isomerize to iminium ion electrophiles first so that they could participate in the next reactions (Scheme 1, Equation 1). According to the intermediate formed in the above reactions, only secondary enamides worked well. Attempted reactions with tertiary enamides failed. It should be noted that Brønsted acid type catalysts are the only compounds that have been discovered to promote these reactions.[8] Moreover, to the best of our knowledge, the reaction of enamide in water as a solvent has not been reported. However, water has been confirmed in a lot of cases to be an ideal solvent for organic reactions due to its advantages of nontoxicity, nonflammability, abundant availability, and inexpensiveness.[9]



Scheme 1. Catalyst-mediated nucleophilic and electrophilic pathway of enamide.

We have been interested in the syntheses of indole derivatives and green chemistry for some years.[10] As a continuing work, we here report a series of novel and ferric nitrate catalyzed regioselective F–C reactions between indoles and tertiary enamides, which were carried out in water at room temperature to offer the C3-alkylated indoles exclusively in moderate to high yields (Scheme 2).



Scheme 2. Ferric nitrate catalyzed F–C reactions of indoles and *tert*-enamide in water.

Results and Discussion

To initiate our study, 1-vinylpyrrolidin-2-one (**1a**) was selected as a model substrate to react with indole (**2a**) in water at room temperature. No reaction was observed in the absence of a catalyst even when the mixture was stirred at 60 °C or tetrabutylammonium bromide (TBAB) was added

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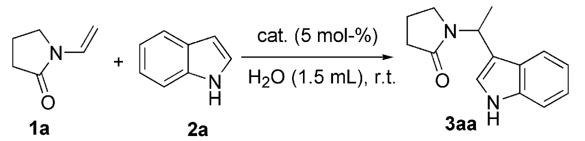
as a phase-transfer catalyst (PTC) (Table 1, Entries 1–3). Then, we investigated the feasibility of Lewis acid and Brønsted acid catalysis. PTSA (*p*-toluenesulfonic acid) was also unable to promote the reaction (Table 1, Entry 4). Some well-documented catalysts[8b] were tested subsequently, but no satisfactory results appeared in these reactions (Table 1, Entries 5–8). With respect to some catalysts investigated, we fortunately found that the reaction could take place in the presence of $FeCl_3$ (Table 1, Entries 9–12) for a 52% yield. When water-soluble catalysts were considered, it was surprising that the reaction performed well with iron(III) salts (Table 1, Entries 12–14) but hardly with iron(II) salts (Table 1, Entries 15 and 16). Among the iron(III) salts investigated, $Fe(NO_3)_3 \cdot 9H_2O$ was found to offer the highest yield of 83% for product **3aa**. In order to explore the effect of the nitrate group on the reaction, $Bi(NO_3)_3 \cdot 5H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, and $Co(NO_3)_2 \cdot 6H_2O$ were also employed. However, no reactions were observed at all in the presence of $Zn(NO_3)_2 \cdot 6H_2O$ or $Co(NO_3)_2 \cdot 6H_2O$ (Table 1, Entries 17–19), $Bi(NO_3)_3 \cdot 5H_2O$ afforded the product in comparable yield. From these experimental data, it is clear that the metal ions play a more important role in these catalytic transformations than their counterparts. Furthermore, studies on the influence of the selected PTCs indicate that tetrabutylammonium iodide (TBAI) was the best one (Table 1, Entries 20–22). Although the addition of TBAI did not give us a better result in screening conditions, the expected adducts were isolated in very low yields without TBAI (see Table 2) as other substituted indoles were introduced.

From these optimized conditions [$Fe(NO_3)_3 \cdot 9H_2O$ (5 mol-%), H_2O (1.5 mL), TBAI (5 mol-%), r.t.], the scope of the reaction was explored by changing the structure of the indoles, as summarized in Table 2. The reaction of **1a** with 2-methyl-1*H*-indole (**2b**) was able to perform smoothly for a 79% yield of **3ab**. When 2-phenyl-1*H*-indole (**2c**) was applied, a longer reaction time was necessary, and nevertheless, a 58% yield of **3ac** could be isolated after 24 h (Table 2, Entry 3). Meanwhile, 4-(benzyloxy)-1*H*-indole (**2d**) could also react well in this catalytic system to afford a 73% yield of desired product **3ad** (Table 2, Entry 4). From these results, we found that the yield decreased slightly with substituents at the 2- or 4-position of indole, possibly as a result of steric effects. As for indoles bearing either electron-releasing (Table 2, Entries 5, 7, 9) or electron-withdrawing groups (Table 2, Entry 6), the reactions with **1a** proceeded effectively to generate the C3-alkylated adducts (82–89%). Noteworthy is that 7-nitroindole underwent alkylation well with **1a** under the same conditions for a 51% yield (Table 2, Entry 8). It was satisfactory that *N*-methylindole performed well in this system (Table 2, Entry 9), although it failed under Brønsted acid catalyzed conditions.[7b] Another *tert*-enamide within our accessibility was tested as well. It was observed that the reaction of *N*-vinyl-ε-caprolactam (**1b**) generally proceeded more slowly and gave a lower yield than 1-vinylpyrrolidin-2-one (Table 2, Entries 10–18). The structure of representative compound **3bf** was confirmed by X-ray single crystal diffraction (Figure 1).[11]

Table 1. Screening of catalysts for the reaction of **1a** with **2a**.



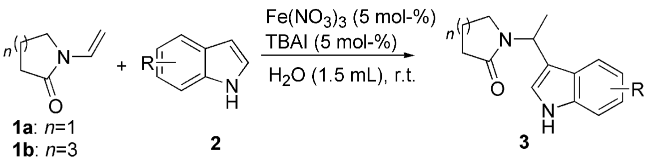
Entry[a]	Catalyst	Time [h]	Yield [%][b]
1	–	12	0
2	–	12	0 [c]
3	TBAB	12	0
4	PTSA[d]	12	0
5	$Cu(OTf)_2$	12	0
6	$Cu(OAc)_2 \cdot H_2O$	12	0
7	$CoCl_2 \cdot 6H_2O$	12	0
8	$Yb(OTf)_3$	12	0
9	$NiCl_2$	12	0
10	$ZnCl_2$	12	0
11	$CeCl_3 \cdot 7H_2O$	12	0
12	$FeCl_3$	7	52
13	$Fe_2(SO_4)_3 \cdot 7H_2O$	7	77
14	$Fe(NO_3)_3 \cdot 9H_2O$	7	83
15	$(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$	12	0
16	$FeSO_4 \cdot 7H_2O$	7	18
17	$Bi(NO_3)_3 \cdot 5H_2O$	7	74
18	$Zn(NO_3)_2 \cdot 6H_2O$	12	0
19	$Co(NO_3)_2 \cdot 6H_2O$	12	0
20	$Fe(NO_3)_3 \cdot 9H_2O$ + TBAB	7	82
21	$Fe(NO_3)_3 \cdot 9H_2O$ + TBAI	7	87
22	$Fe(NO_3)_3 \cdot 9H_2O$ + SDS[e]	7	71

[a] Reaction conditions: **1a** (0.25 mmol), **2a** (0.50 mmol), catalyst (5 mol-%), H_2O (1.5 mL), PTC (5 mol-%) at room temperature. [b] Yield of isolated product after flash chromatography. [c] At 60 °C. [d] PTSA = *p*-toluenesulfonic acid. [e] SDS = sodium dodecyl sulfate.

However, the protocol was limited when other *N*-vinyl compounds were introduced. For example, *N*-vinylcarbazole did not perform under the standard conditions. Other electron-rich aromatics that did also perform smoothly in this system are listed in Figure 2.

These data led us to explore the reaction mechanism. In comparison with the structures of three electron-rich olefin substrates, we think that the carbonyl group in the enamide plays an important role in this kind of F–C reaction. We tried to extract some valuable information from the IR stretching frequencies of the C=O group from 1-vinylpyrrolid-in-2-one in the presence of $Fe(NO_3)_3 \cdot 9H_2O$. The absorption peak of the carbonyl group in a mixture of **1a** and $Fe(NO_3)_3 \cdot 9H_2O$ (1 equiv.) was redshifted from 1673 cm^{-1} (for **1a**) to 1640 cm^{-1} (intermediate **A**; see their spectra in the Supporting Information). This is a convincing evidence for the interaction between iron(III) and the carbonyl group from enamide, which is consistent with the fact that electron-rich alkenes without a carbonyl group did not react with indoles under the same conditions. Additionally, the wide and strong absorption at 1640 cm^{-1} implied the existence of a delocalized π bond in the [CCNCO] system. It also meant that the C=C bond might be activated by the iron(III) ion at the same time. Thus, hydration would read-

Table 2. Ferric nitrate catalyzed F–C alkylation of indoles and *tert*-enamides.



Entry[a]		Substrates R		Time [h]	Product	Yield [%][b]
1	**1a**	H	**2a**	7	**3aa**	87
2		2-Me	**2b**	6	**3ab**	79 (67)[c]
3		2-Ph	**2c**	24	**3ac**	58
4		4-BnO	**2d**	11	**3ad**	73
5		5-Me	**2e**	8	**3ae**	87
6		5-Br	**2f**	7	**3af**	82 (21)[c]
7		7-Me	**2g**	7	**3ag**	89
8		7-NO_2	**2h**	24	**3ah**	51
9		*N*-Me	**2i**	6	**3ai**	88 (36)[c]
10	**1b**	H	**2a**	8	**3ba**	74
11		2-Me	**2b**	12	**3bb**	61
12		4-Me	**2j**	12	**3bj**	58
13		4-BnO	**2d**	12	**3bd**	31
14		5-Me	**2e**	12	**3be**	69
15		5-Br	**2f**	12	**3bf**	50
16		6-Me	**2k**	9	**3bk**	74
17		7-Me	**2g**	12	**3bg**	74
18		*N*-Me	**2i**	10	**3bi**	77

[a] Reaction conditions: **1** (0.5 mmol), **2** (1.0 mmol), catalyst [$Fe(NO_3)_3\cdot 9H_2O$ 5 mol-% + TBAI 5 mol-%], H_2O (1.5 mL) at room temperature. [b] Yield of isolated product after flash chromatography. [c] Isolated yield without addition of TBAI.

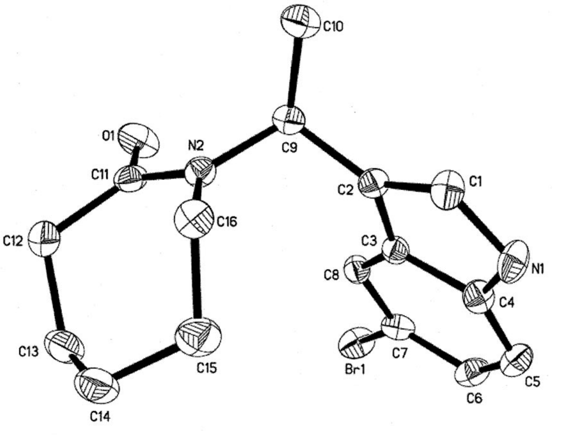


Figure 1. Crystal structure of **3bf**.

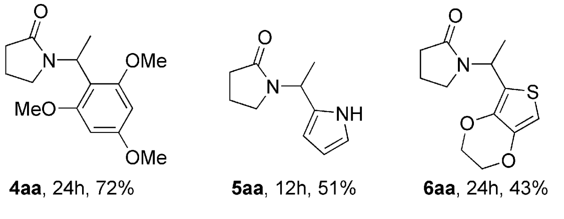


Figure 2. Ferric nitrate catalyzed F–C reaction of other aromatics and *tert*-enamide.

ily occur on the highly polarized C=C bond. The confirmative evidence was achieved by ^{13}C NMR spectroscopic analyses. The typical peaks of the sp^3 carbon formed in situ appeared at $\delta = 69$ and 16 ppm in the presence of the catalyst (1 equiv.), whereas the peaks of the sp^2 carbon in **1a** appeared at 126 and 94 ppm (Figure 3).[12] To further verify our assumed mechanism, we separated the product from the reaction of indole and **1a** in deuterated water. Just as we expected (Scheme 3), the deuterium from the solvent appeared in the product (characteristic data and spectra, see: **3aa′** in the Supporting Information), which proved the hydration of the highly polarized C=C bond.

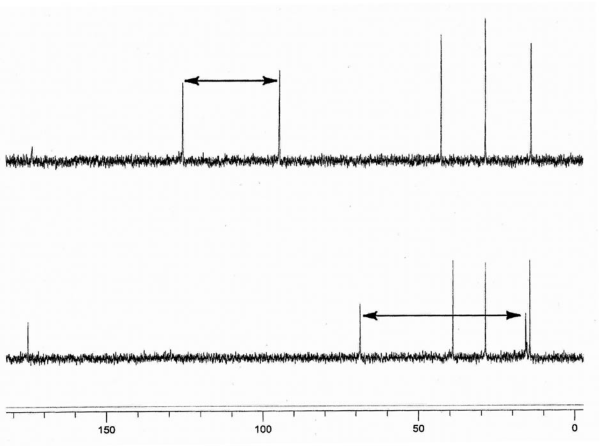
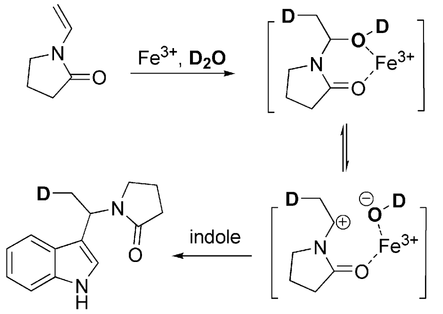
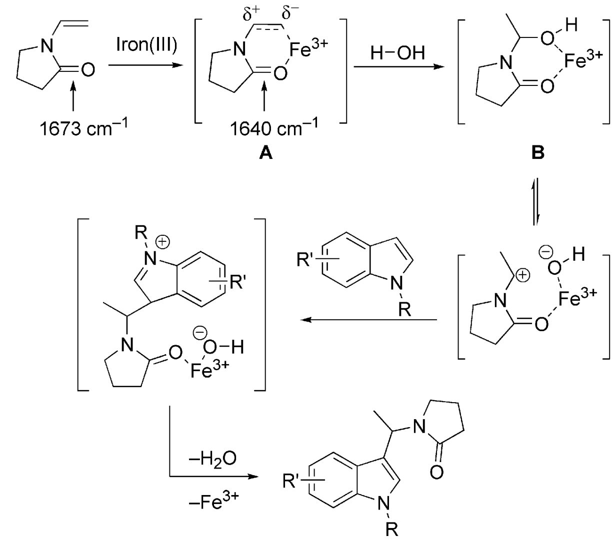


Figure 3. ^{13}C NMR spectra of **1a** (top) and a mixture of **1a** and the catalyst (1 equiv.; bottom) in D_2O.



Scheme 3.

Here, we can understand the whole mechanism as follows (Scheme 4):[13] With the coordination of the carbonyl group, the iron(III) ion with a positive charge activates and polarizes the C=C bond (intermediate **A**). Hydration of the C=C bond subsequently occurs to form intermediate **B**.[14] Under these circumstances, iron(III) activates the hydroxy group[15] to form a stable carbocation, which is attacked further by C3 of indole to form a new carbon–carbon bond. Electron transfer and hydrogen elimination easily lead to the formation of the final product.[16]



Scheme 4. Plausible mechanism for Fe^{III} catalysis.

Conclusions

In summary, we have described a ferric nitrate catalyzed F–C alkylation of indoles with *tert*-enamides in water at room temperature. This atom-economical and environmentally friendly procedure uses an inexpensive catalyst with low loadings and establishes a new Lewis acid catalyzed F–C alkylation between indoles with electron-rich olefins. The fact that the coordinative group promotes the activation of the electron-rich C=C bond in the presence of a catalyst allows the substrate scope to be extended to other olefins in F–C alkylations. Applications of this methodology to other reactions are currently under investigation in our laboratory.

Experimental Section

General: Melting points were measured with an Electrothermal digital melting point apparatus. IR spectra were recorded with a Varian FT-1000 spectrophotometer by using KBr optics. ^1H and ^{13}C NMR spectra were recorded with a Varian INOVA 300 or 75 or 100 MHz spectrometer by using $CDCl_3$ or [D$_6$]DMSO as solvent and TMS as an internal standard. High-resolution mass spectra were obtained by using a Microma GCT-TOF instrument. X-ray diffraction was performed with a Rigaku Mercury CCD area detector with graphite monochromated Mo-K_α radiation.

Typical Experimental Procedure for the Reaction of Indole with Enamide: Indole (0.50 mmol), $Fe(NO_3)_3\cdot 9H_2O$ (5 mol-%), TBAI (5 mol-%), and enamide (1.0 mmol) were added into a flask. H_2O (1.50 mL) was then added, and the mixture was vigorously stirred at room temperature until indole was completely consumed (checked by TLC) or until an appropriate time had passed. After completion of reaction, the product was extracted with ethyl acetate, and the organic phase was dried with anhydrous Na_2SO_4. The solvent was removed under the reduced pressure, and the residue was purified by flash column chromatography (ethyl acetate/petroleum ether) to afford the pure product.

1-[1-(1*H*-Indol-3-yl)ethyl]pyrrolidin-2-one (3aa): Yield: 99 mg (87%). White solid, m.p. 165–167 °C. IR (KBr): $\tilde{\nu}$ = 3243, 3165, 3107, 2972, 2876, 1659, 1490, 1440, 1288, 1198, 751 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.60 (d, J = 6.9 Hz, 3 H, CH_3), 1.86–2.04 (m, 2 H, CH_2), 2.38–2.46 (m, 2 H, CH_2), 2.85–2.91 (m, 1 H), 3.23–3.38 (m, 1 H), 5.78 (q, J = 6.6 Hz, 1 H, CH), 7.08–7.12 (m, 2 H, ArH), 7.18–7.22 (m, 1 H, ArH), 7.37 (d, J = 8.1 Hz, 1 H, ArH), 7.62 (d, J = 7.8 Hz, 1 H, ArH), 8.32 (br., s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.8, 137.0, 126.9, 122.8, 122.6, 120.3, 119.9, 116.4, 111.6, 43.1, 42.7, 32.2, 18.2, 17.1 ppm. HRMS: calcd. for $C_{14}H_{16}N_2O$ 228.1263; found 228.1266.

Supporting Information (see footnote on the first page of this article): Copies of the ^1H and ^{13}C NMR spectra of all products and some information about the mechanism.

Acknowledgments

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[11] CCDC-756632 (for **3bf**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Structural parameters for **3bf**: data collection: Rigaku Mercury CCD area detector; crystal size: $0.60 \times 0.60 \times 0.50$ mm^3. $C_{16}H_{21}BrN_2O_2$, M_r = 353.26, monoclinic, space group $P2_1/n$, a = 10.3238(16) Å, b = 8.4856(13) Å, c = 18.447(3) Å, α = 90.00°, β = 93.119(4)°, γ = 90.00°, V = 1613.7(4) Å^3, Z = 4, $D_{calcd.}$ = 1.454 g cm^{-3}, $R[I > 2\sigma(I)]$ = 0.0400, $wR[I > 2\sigma(I)]$ = 0.0919.

[12] Due to the paramagnetic properties of iron(III), no distinguished NMR spectra could be provided. Thus, in order to get the important information about the interaction of the vinyl group and the catalyst, $Bi(NO_3)_3 \cdot 5H_2O$, which also has been proved to be an efficient catalyst (Table 1, Entry 17), was used instead of $Fe(NO_3)_3 \cdot 9H_2O$ in the ^{13}C NMR spectroscopic analysis. We also achieved in situ ^{13}C NMR information of the mixture of 1-vinylimidazole and $Bi(NO_3)_3 \cdot 5H_2O$ (1 equiv.) in D_2O (see Supporting Information): there was no significant shift in the C=C bond, which also explains why the reaction between 1-vinylimidazole and indole did not perform under this system. The catalyst may coordinate to the nitrogen atom of 1-vinylimidazole in the absence of the C=O group, and the catalyst could not activate the C=C bond effectively.

[13] A similar reaction mechanism was proposed by Lin et al., although not enough evidence was presented, see: W. B. Wu, J. M. Xu, Q. Wu, D. S. Lv, X. F. Lin, *Adv. Synth. Catal.* **2006**, *348*, 487–492.

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