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Iron-Catalyzed Acyl Migration of Tertiary α-Azidyl Ketones: Synthetic Approach toward Enamides and Isoquinolones

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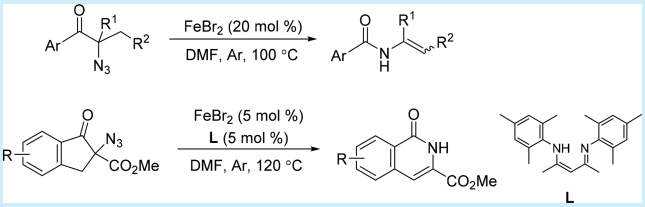
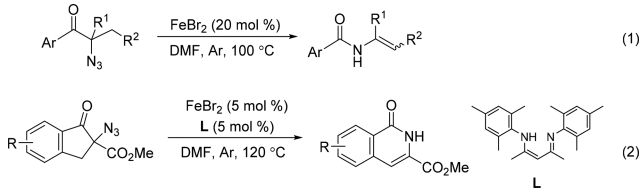
Supporting Information

ABSTRACT: This paper reports that tertiary α-azidyl phenyl ketones can be transformed into enamides by treatment with $FeBr_2$ at elevated temperature in DMF. The reaction proceeds via 1,2-benzoyl migration from α-carbon to the nitrogen atom, accompanied by expulsion of a nitrogen molecule. This protocol is suitable for the synthesis of *N*-(cyclopent-1-en-1-yl)benzamides, *N*-(cyclohex-1-en-1-yl)benzamides, and *N*-benzoyl-α-methyl enamines and provides a convenient approach toward isoquinolones.



Organic azides are important compounds that have manifold applications in organic synthesis.[1] Recently, the transition-metal-catalyzed amination reactions with azides as precursors have emerged to prominence because they provide highly effective and atom-economic approaches toward nitrogen-containing compounds.[2] In this context, much attention has been paid to azide-involved amination reactions with iron as catalyst.[3−6] From the point view of modern synthesis and catalysis, iron constitutes an ideal catalyst candidate because of its high earth abundance, low cost, and nontoxicity, and the versatile capacities of iron salts and complexes as catalyst have been well demonstrated by recent studies.[7] It has been proven that iron is highly capable of catalyzing the C−H amination with azides as the nitrogen source,[3,4] and it can also enable the aminations of alkenes and alkynes[5] as well as thioethers and sulfoxides.[6] As a continuation of our interest in the azide-involved C−N forming reactions,[8] recently, we found that tertiary α-azidyl phenyl ketones can be transformed into enamides by treatment with $FeBr_2$ at elevated temperature in DMF (Scheme 1, (1)). The reaction proceeded via 1,2-benzoyl migration to the nitrogen atom, accompanied by expulsion of a nitrogen molecule. This protocol can be applied to the preparation of isoquinolone compounds (Scheme 1, (2)). Herein, we report this result.

Scheme 1. Iron-Catalyzed 1,2-Acyl Migration of Tertiary α-Azidyl Ketones



At the initial stage of this study, we found that when treated with 20 mol % of $FeBr_2$ at 100 °C in DMF under an argon atmosphere, compound **1a** can be converted efficiently into enamide **2a** in high yield (Table 1, entries 3 and 4). Inferior results were obtained at higher or lower temperature (entries 1 and 6). The optimal loading level of $FeBr_2$ was found to be 20%. The reaction also took place in acetonitrile, but it hardly occurred when toluene or DMSO was used as the solvent (entries 8 and 9). Apart from $FeBr_2$, other ferrous salts, such as $FeCl_2$, $Fe(OTf)_2$, $Fe(OAc)_2$, and $Fe(acac)_2$, exhibited little or no catalytic activity (entries 15−18). The reaction was also explored in the presence of ligands such as L1, L2, or L3, but in these cases, the yields of **2a** were noticeably lower (entries 11−13) compared with that under ligand-free conditions.

Enamides belong to an important class of organic compounds that serve as versatile intermediates in organic synthesis.[9] Numerous studies have been made to gain access to this useful structural motif.[10−17] Synthesis of enamides mostly involves (1) the reductive acylation of ketoximes,[10] (2) acylation of the in situ formed imine intermediates,[11] (3) condensation of amides with ketones,[12] (4) transition-metal-catalyzed C−N coupling of vinyl electrophiles[13] or vinyl nucleophiles[14] with amidating agents, (5) isomerization of allylamides,[15] (6) hydroamidation of alkynes,[16] and (7) addition to ynamides.[17] Several new strategies have also been reported recently to achieve this goal.[18] We envisioned that the present iron-mediated rearrangement of α-azidyl ketones might also be applied to the synthesis of enamides. In this regard, the optimal conditions (Table 1, entry 5) were then used upon differently substituted α-azidyl ketones, and the result is illustrated in Scheme 2.

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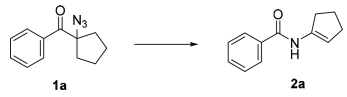
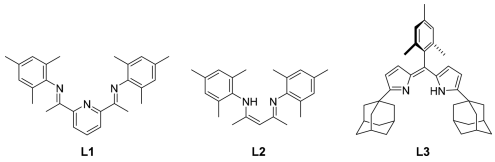
Table 1. Screening of Reaction Conditions[a]

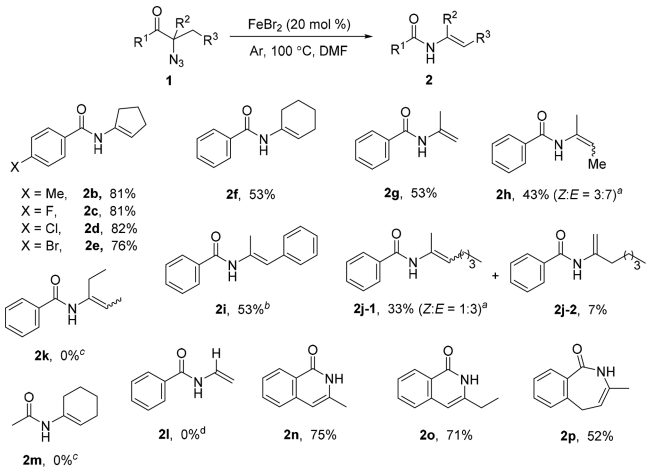


entry	[Fe^{II}][b] (20 mol %)	solvent	temp (°C)	time (h)	yield of **2a** (%)
1	$FeBr_2$	DMF	80	16	14
2	$FeBr_2$	CH3CN	80	18	43
3	$FeBr_2$	DMF	100	8	78
4	$FeBr_2$	DMF	100	6	83
5	$FeBr_2$[c]	DMF	100	6	83
6	$FeBr_2$	DMF	120	2	40
7	$FeBr_2$	CH_3CN	100	8	63
8	$FeBr_2$	toluene	100	8	4[d]
9	$FeBr_2$	DMSO	100	8	9[d]
10	$FeBr_2$ (10)	DMF	100	8	62
11	$FeBr_2$ (10)	DMF	100	8	21[e]
12	$FeBr_2$ (10)	DMF	100	8	52[f]
13	$FeBr_2$ (10)	DMF	100	8	27[g]
14	$FeBr_2$ (30)	DMF	100	6	56
15	$Fe(OTf)_2$	DMF	100	8	NR[h]
16	$FeCl_2$	DMF	100	8	7[d]
17	$Fe(OAc)_2$	DMF	100	8	NR
18	$Fe(acac)_2$	DMF	100	8	NR
19		DMF	100	8	NR



[a]The reaction was conducted on 0.2 mmol scale in 2 mL of solvent under an argon atmosphere. [b]20 mol % of ferrous salt was used unless otherwise indicated. [c]The reaction was conducted on 0.5 mmol scale in 5.5 mL of solvent. [d]Most of **1a** was recovered. [e]In the presence of 10 mol % of L1. [f]In the presence of 10 mol % of L2. [g]In the presence of 10 mol % of L3. [h]No reaction took place.

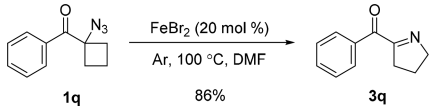
Scheme 2. Scope of the $FeBr_2$-Catalyzed Reaction for the Synthesis of Enamides from α-Azidyl Ketones



[a]The configurations were determined by comparing the NMR spectra with those found in ref 15d. See the Supporting Information. [b]The configuration was determined on the basis of NOE of ^1H NMR spectra. [c]No reaction took place. [d]S. M. decomposed.

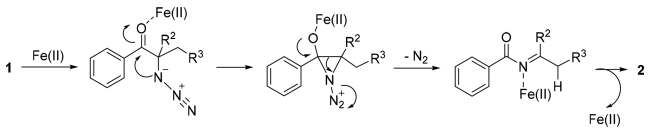
As shown in Scheme 2, this protocol is applicabe to the preparation of *N*-(cyclopent-1-en-1-yl)benzamides (**2b–e**) and *N*-(cyclohex-1-en-1-yl)benzamides (**2f**). Open-chain tertiary α-azidyl phenyl ketones with at least one α-methyl substituent enamides (**2g–j**) also be converted into the corresponding enamides, albeit in lower yield. The present method has the merits in that the precursors are easily accessible, and the reaction is atom-economical. However, this procedure did not work for nontertiary α-azidyl phenyl ketones (**2l**), aliphatic α-azidyl ketones (**2m**), or substrates lacking α-methyl substituent (**2k**). It is interesting to see that for the reactions of **1h**, **1i**, and **1j** the formation of the double bond is highly regioselective to deliver predominantly the more substituted alkenes. The *E*-selectivity was also observed for these reactions. When 2-azido-2,3-dihydro-1*H*-indenone or 2-azido-3,4-dihydronaphthalen-1(2*H*)-one was used as the substrate, the corresponding isoquinolone (**2n** and **2o**) and 2,5-dihydro-1*H*-benzo[c]azepin-1-one (**2p**) products were generated in good yields. This protocol was also applied to compound **1q**, but in this case, no enamide product was obtained; instead, imine **3q** was generated in 86% yield (Scheme 3).

Scheme 3. Reaction of (1-Azidocyclobutyl)(phenyl)-ketone



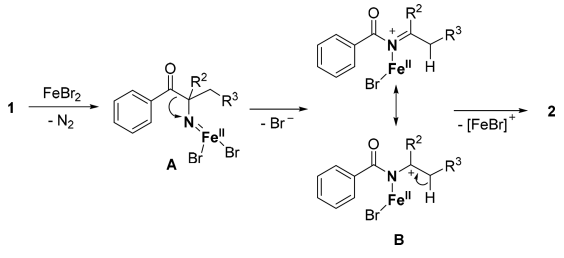
This acyl-migration rearrangement is interesting from a mechanistic point of view. It is analogous to the Schmidt rearrangement in reaction pattern[19] and might follow the pathway shown in Scheme 4. However, our control experiment

Scheme 4. Possible Schmidt-Type Mechanism for the Present Reactions



indicated that this transformation cannot be effected through the action of commonly used Lewis acids, such as $FeCl_3$, $BF_3{\cdot}OEt_2$, $TiCl_4$, $Zn(OTf)_2$, and $Sc(OTf)_3$ (see Table S2), whereas these acids should be superior to $FeBr_2$ for the Schmidt reaction. Besides the Schmidt-type mechanism, there is another possibility that acyl migration takes place through an iron–nitrene intermediate (Scheme 5). Recent studies demonstrate that iron salts and complexes can form metal–nitrene species with the azidyl group like intermediate **A**.[3,4] These iron–

Scheme 5. Proposed Mechanism Involving Iron–Nitrene Intermediate



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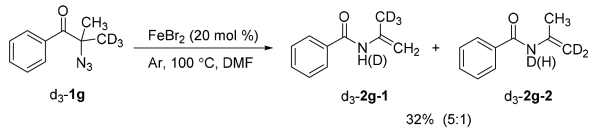
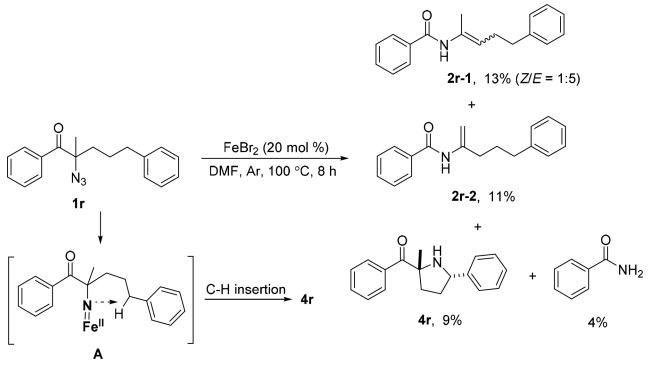
nitrene species are electrophilic-like nitrenes. As nitrenes have a strong tendency to undergo 1,2 migration from the carbon to nitrogen atom, it is reasonable to assume that analogous migration process could occur for intermediate **A**. The kinetic isotope experiment showed that when compound d_3-**1g** was subjected to the reaction conditions, it reacted to afford two products, d_3-**2g-1** and d_3-**2g-2**, in a ratio of 5:1 (Scheme 6).

Scheme 6. Kinetic Isotope Experiment with d_3-1g



This result is in accordance with both of these two mechanisms. However, the reaction of **1q**, as shown in Scheme 3, lent support to the iron−nitrene mechanism as in this case, it is the methylene, rather than the acyl group, that migrated to the nitrogen atom, probably because of the ring strain. Imine **3q** cannot be formed via Schmidt reaction. Further evidence supporting the iron−nitrene mechanism came from the reaction of **1r** (Scheme 7). It was anticipated that if the

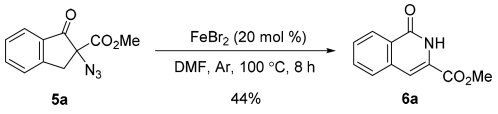
Scheme 7. Evidence Supporting the Iron−Nitrene Mechanism



reaction proceeded through an iron-nitrene intermediate, intramolecular C−H insertion would occur for compound **1r** to provide a five-membered ring. Indeed, when **1r** was subjected to the reaction conditions, **4r** was generated along with enamide products.

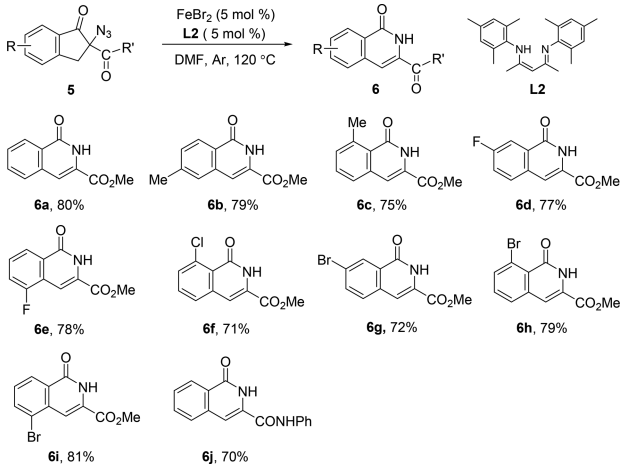
As illustrated in Scheme 2, when 2-azido-2,3-dihydro-1*H*-indenones were used as the substrates, isoquinolone products were generated in good yields. Isoquinolone is an important structural motif that appears in many natural products and pharmaceuticals,[20] and its construction has long been of interest to synthetic organic chemists.[21] It was expected the present method would provide a new approach toward isoquinolone compounds. With this consideration in mind, we applied this protocol to 2-methoxycarbonyl-substituted **5a** to examine its scope (Scheme 8). As expected, the isoquinolone product **6a** was obtained, but the yield was not high.

Scheme 8. Reaction of 4a under the Catalysis of $FeBr_2$



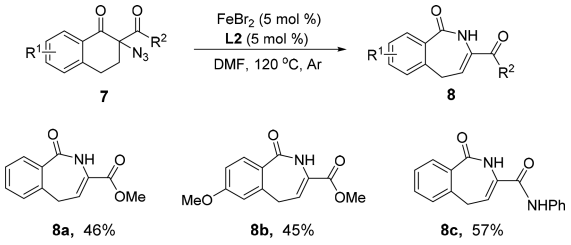
Subsequent exploration of the reaction conditions (see Table S3) showed that when ligand L2 was used together with $FeBr_2$ the yield of **6a** can be considerably improved. As such, **6a** was obtained in 80% yield at the catalyst loading of 5 mol % when the reaction temperature was raised to 120 °C. The latter conditions are applicable to the preparation of isoquinoline-3-carboxylates and isoquinoline-3-carboxamides, and the yields were good in general (Scheme 9). It is noteworthy that this

Scheme 9. Preparation of Substituted Isoquinolones with the Modified Protocol



protocol can be applied to the preparation of isoquinolones bearing a substituent varying in position at the phenyl ring, which may be difficult with other methods. In addition to isoquinoline compounds, functionalized 2-benzazepin-1-ones[22] can be prepared in an analogous manner, albeit in lower yields (Scheme 10).

Scheme 10. Preparation of 2-Benzazepin-1-ones



To further examine the scope of this method, the conditions of $FeBr_2$/L2 were next applied to several other 2-azidyl 1,3-dicarbonyl compounds (**9**). As shown in Scheme 11, among the substrates tested, **9a−e** were transformed into the corresponding enamides in moderate yields, while the desired reaction did not occur for other substrates. The low yield for **10a−d** might be caused by the decomposition of these compounds, as benzamide was generated as a byproduct in all these cases. The low yield of **10e**, on the other hand, is due to incomplete conversion as well as its decomposition.

In summary, we have demonstrated that tertiary α-azidyl ketones can be converted into enamides via denitrogenative 1,2-acyl migration by the catalysis of $FeBr_2$. The reactions provide a convenient approach toward *N*-(cyclopent-1-en-1-yl)benzamides, *N*-(cyclohex-1-en-1-yl)benzamides, and *N*-benzoyl α-methyl enamines. This method is well suitable for

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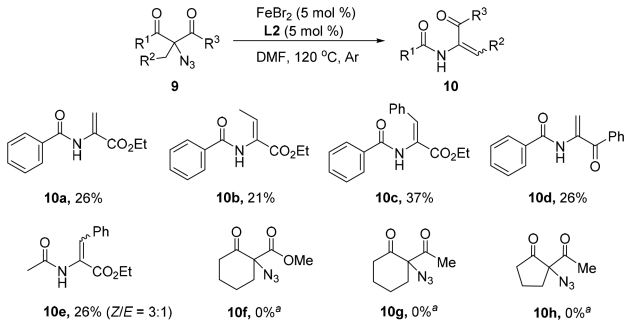
Scheme 11. Further Test of the Scope of This Method



[a]Substrate decomposed.

the synthesis of isoquinolone compounds. Further work is being done in our laboratory to explore milder reaction conditions to enhance the synthetic usefulness of this method.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b00409.

General experimental procedures, tables illustrating screening of the reaction conditions, characterization data for the substrates and products, ^{1}H NMR and ^{13}C NMR spectra of the substrates and products (PDF)

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Notes

The authors declare no competing financial interest.

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