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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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Silver-Catalyzed Long-Distance Aryl Migration from Carbon Center to Nitrogen Center

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Supporting Information

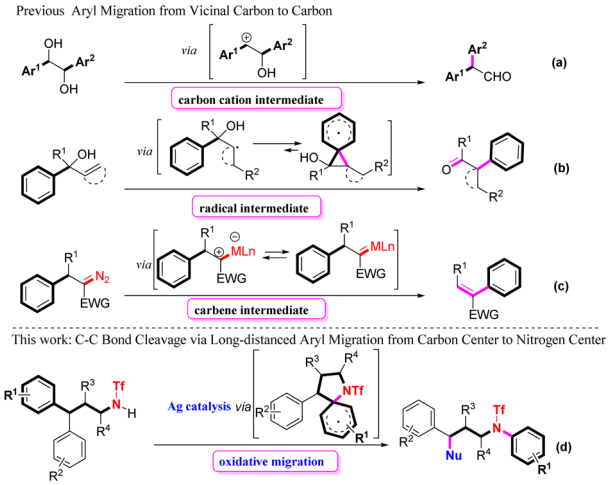
ABSTRACT: Selective cleavage of an inert C−C bond followed by C−O/N bond formation through a long-distance aryl migration from a carbon to a nitrogen center via Ag catalysis is reported. The migration products were easily converted into γ-hydroxy amines and tetrahydroquinoline derivatives in quantitative yields. Preliminary mechanistic studies indicated a radical pathway.

Selective C−C bond activation/cleavage has attracted much attention in recent years.[1] Not only is it one of the most challenging themes in fundamental organic chemistry, but it also represents a powerful, straightforward, and atom-economic strategy for constructing new organic compounds through a completely new pathway based on reorganization of the skeletons of easily available compounds, differentiating it from conventional organic syntheses.[1] During the past few decades, many achievements in transition-metal-catalyzed C−C cleavage have been made, starting from strained and unstrained compounds.[2,3] In the absence of transition metal catalysts, C−C could be cleaved and transformed through radical[4] and cationic intermediates.[5] Among different strategies to approach direct C−C cleavage of unstrained molecules, the migration of carbon-based groups is common and important to facilitate the C−C cleavage and new C−C formation.[6]

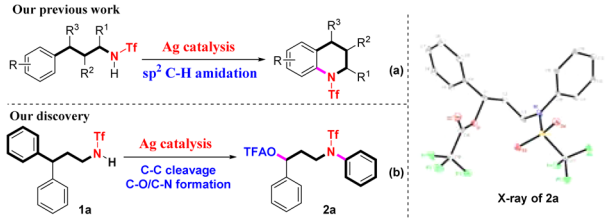
In general, group migration takes place only at carbon centers adjacent to carbon cations,[5] radicals,[6c−f] or carbenes[3a] (Scheme 1). Beautiful examples of long-distance (over four carbons) migrations have been reported by Pohmakotr,[6g] Liang,[6h] Tchabanenko,[6i] Uneyama,[6j] and others.[6a,b] However, group migration from a carbon to a nitrogen center is scarcely reported,[7] and in particular, long-distance aryl migration from a carbon to a nitrogen center has never been approached. Herein we demonstrate an unusual Ag-catalyzed long-distance aryl migration from a carbon to a nitrogen center (Scheme 1d).

In our previous studies, we observed direct annulation through sp^2 C−H amidation via Ag catalysis (Scheme 2a).[8] Yokoyama and co-workers also reported the formation of tetrahydroquinoline derivatives from a similar triflic amide promoted by irradiation.[9] Later on, we planned to explore asymmetric C−N formation through desymmetrization via Ag catalysis with chiral ligands. Accidentally, we found phenyl migration product **2a**, which was unambiguously confirmed by X-ray crystallography (Scheme 2b). We proposed that both annulation and migration products might be generated from the same N-centered radical or cation as a key intermediate. From those intermediates, the dearomatization process would take place to form the σ-complexes (either σ-radical or σ-cation complex) when aryl group was present at the proper position, which could induce a completely different chemistry from the same starting materials. Indeed, both intra- and intermolecular dearomatization of the heterocycles as well as electron-rich phenol derivatives through radical or cationic processes has been well studied, thus supporting the possibility for our hypothesis, although the dearomatization of common benzene

Scheme 1. New Development of C−C Cleavage via Ag-Catalyzed Long-Distance Aryl Migration under Oxidative Conditions



Scheme 2. Different Chemistry of Triflic Amides



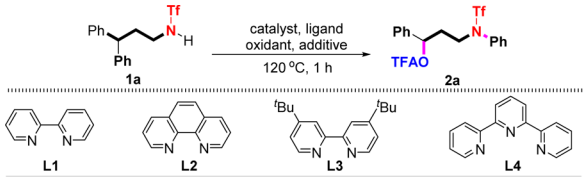
Received: September 30, 2015
Published: November 2, 2015

DOI: 10.1021/jacs.5b10267
J. Am. Chem. Soc. 2015, 137, 14586−14589

derivatives was scarcely reported.[10] Therefore, we developed this long-distance aryl migration.

With this idea in mind, we first screened the conditions to promote such a migration with **1a** as a model (Table 1).

Table 1. Ag-Catalyzed Long-Distance Aryl Migration of 1a under Different Conditions[a]



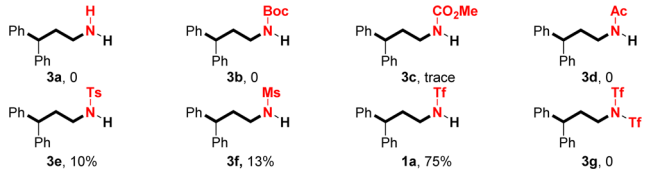
entry	catalyst (20 mol%)	ligand (20 mol%)	oxidant (2.0 eq)	additive (2.0 eq)	solvent	yield[b] (%)
1	AgOAc	L1	-	-	DCE	0
2	AgOAc	L1	Oxone	-	DCE	0
3	AgOAc	L1	$PhI(OAc)_2$	-	DCE	0
4	AgOAc	L1	$K_2S_2O_8$	-	DCE	0
5	**AgOAc**	L1	**$PhI(OTFA)_2$**	-	DCE	31%
6	$Pd(OAc)_2$	L1	$PhI(OTFA)_2$	-	DCE	Trace
7	CuOAc	L1	$PhI(OTFA)_2$	-	DCE	0
8	AuCl	L1	$PhI(OTFA)_2$	-	DCE	0
9	Ag_2O	L1	$PhI(OTFA)_2$	-	DCE	29%
10	$AgNO_3$	L1	$PhI(OTFA)_2$	-	DCE	17%
11	Ag_2CO_3	L1	$PhI(OTFA)_2$	-	DCE	28%
12	AgOAc	L2	$PhI(OTFA)_2$	-	DCE	37%
13	AgOAc	**L3**	$PhI(OTFA)_2$	-	DCE	38%
14	AgOAc	L4	$PhI(OTFA)_2$	-	DCE	21%
15	AgOAc	L3	$PhI(OTFA)_2$	Cs_2CO_3	DCE	12%
16	AgOAc	L3	$PhI(OTFA)_2$	KO^tBu	DCE	36%
17	AgOAc	L3	$PhI(OTFA)_2$	Li_2CO_3	DCE	60%
18	AgOAc	L3	$PhI(OTFA)_2$	**K_2CO_3**	DCE	65%
19	AgOAc	L3	$PhI(OTFA)_2$	K_2CO_3	**DCE/PhCl**	**75%(70%)**[c]

[a]Reaction conditions: substrate (0.1 mmol), catalyst (20 mol%), ligand (20 mol%), oxidant (2.0 equiv), additive (2.0 equiv), dichloroethane (DCE) (2.0 mL), 120 °C, 1 h. [b]The yield was determined by ^1H NMR of the crude reaction mixture with CH_2Br_2 as internal standard. [c]Isolated yields. For more details, see Tables S1−S5 in the Supporting Information.

According to our studies, such a long-distance aryl migration only took place under oxidative conditions and Ag catalyst was critical to promote the efficacy. Thus, different oxidants were tested in the presence of AgOAc as the catalyst and 2,2′-bipyridine (**L1**) as the ligand (entries 2−5). $PhI(OTFA)_2$ was found to be the only oxidant to produce the desired migration product **2a** in 31% yield (entry 5). Other metal catalysts, including Pd, Cu, and Au, were also screened, but most of them were found to be insufficient or to have a quite low efficacy (entries 6−8). Different Ag salts were examined but did not show better performance (entries 9−11). To promote the efficacy, various ligands were evaluated (entries 12−14). 4,4′-Di(*tert*-butyl)-2,2′-bipyridine (**L3**) was found to the best and gave the desired product **2a** in 38% yield (entry 13). Different bases were also screened (entries 15−18). Lithium carbonate and potassium carbonate were found to be efficient (entries 17 and 18), while cesium carbonate and potassium *tert*-butoxide had diminished efficiency (entries 15 and 16). These results indicated that the proper base efficiently deprotonated N−H to facilitate the oxidation of amide to N radical or cation. Different solvents, including PhCl, DCE, dioxane, and so on, were screened, but only DCE worked well (Supporting Information, Table S5, entry 2). We found that the addition of PhCl as co-solvent dramatically improved the yield to 75% (entry 19).

With the optimized conditions in hand, we first evaluated different functionalities on nitrogen atom (Scheme 3), including free amine (**3a**), carbamates (**3b** and **3c**), acetamide (**3d**), and sulfonamides (**3e**, **3f**, and **1a**). However, we found

Scheme 3. Evaluating Different Amides[a]

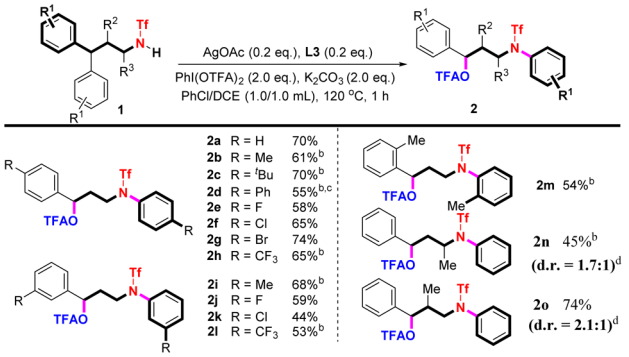


[a]Reaction conditions: substrate (0.1 mmol), AgOAc (20 mol%), **L3** (20 mol%), $PhI(OTFA)_2$ (2.0 equiv), K_2CO_3 (2.0 equiv), PhCl/DCE (1.0 mL/1.0 mL), 120 °C, 1 h. The yield was determined by ^1H NMR of the crude reaction mixture with CH_2Br_2 as internal standard.

that only the sulfonamides performed the migration, while Ts- or Ms-protected amides (**3e**, **3f**) gave poor conversions. Presumably, the strong electron-withdrawing ability of the Tf group enhanced the acidity of the NH group, which could be easily deprotonated by the proper bases and further coordinated to the Ag center. Such an Ag complex could be oxidized to Ag(II) (maybe Ag(III)), which further generated the electron-deficient N-centered radical. This radical attacked the phenyl ring to form five-membered spiro radical σ-complexes. To prove the importance of N−H in amide, the substrate **3g** was tested, and no desired product was obtained at all.

We further extended this type of aryl migration to various symmetric γ,γ-diaryl-substituted triflic amides (Table 2).

Table 2. Ag-Catalyzed Aryl Migration of Symmetrical γ,γ-Diaryl-Substituted Triflic Amides[a]



[a]Reaction conditions: substrate (0.1 mmol), AgOAc (20 mol%), **L3** (20 mol%), $PhI(OTFA)_2$ (2.0 equiv), K_2CO_3 (2.0 equiv), PhCl/DCE (1.0 mL/1.0 mL), 120 °C, 1 h; Yields of isolated products. [b]Yields of isolated corresponding alcoholysis products, which were easily formed upon purification by flash column chromatography (silica gel). [c]120 °C, 10 h. [d]Diastereomer ratio was determined by ^1H NMR.

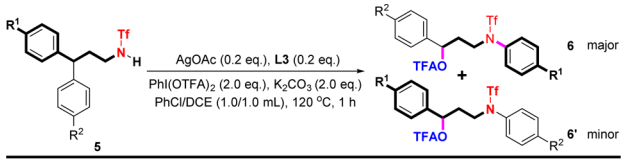
Substrates bearing electron-rich groups at the *para*-position of the aryl ring, including Me (**1b**), ^{t}Bu (**1c**), and Ph (**1d**) were tested, and the desired migration products were afforded in moderate to good yields (**2b**−**2d**). However, strong electron-donating groups containing heteroatoms, for example MeO and Me_2N, induced decomposition of the starting materials under this oxidation condition. Meanwhile, substrates bearing electron-deficient groups at the *para*-position, including F (**1e**), Cl (**1f**), Br (**1g**), and CF_3 (**1h**), gave the desired migration products with comparable efficacy (**2e**−**2h**). Substrates with *meta*-substituents also worked as migration groups (**1i**−**1l**), giving the corresponding products in moderate yields (**2i**−**2l**). A bulkier substrate with an *ortho*-tolyl migrating group (**1m**) also provided the migration product (**2m**) in an

DOI: 10.1021/jacs.5b10267
J. Am. Chem. Soc. 2015, 137, 14586−14589

acceptable yield. These results indicated that steric hindrance on the aryl ring had a slight effect while the electronic property did not have the regular effects. Moreover, the migration of **10**, with a β-methyl substituent of triflic amide, performed well, giving a 74% yield of **2o**. However, the yield of **1n**, with methyl group adjacent to the amide, was reduced to 45%, albeit over a longer time, further proving the steric effect on this migration.

Furthermore, we investigated the migrating ability of different aryl groups in unsymmetrical triflic amides (Table 3). Phenyl and 4-chlorophenyl in **5a** was first examined, and the

Table 3. Ag-Catalyzed Aryl Migration of Unsymmetrical γ,γ-Diaryl-Substituted Triflic Amides[a]



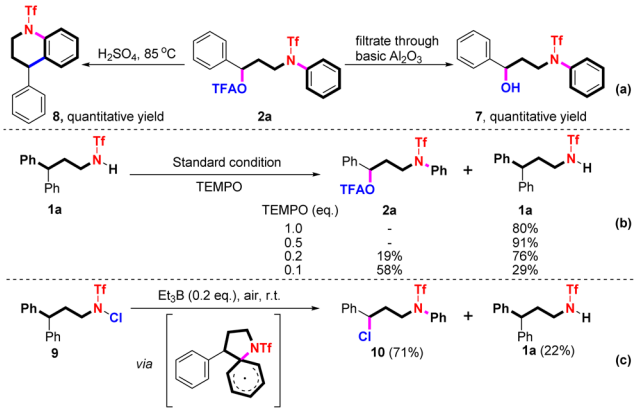
Entry	Substrate	R^1	R^2	Major migrating group	Yield (%)	Ratio[d]
1	**5a**	H	Cl	Ph	65[b]	1.4/1
2	**5b**	H	CF_3	Ph	49[b,c]	5.9/1
3	**5c**	CH_3	CF_3	*p*-$CH_3C_6H_4$	58[b,c]	25/1
4	**5d**	*t*-Bu	CF_3	*p*-(*t*-Bu)C_6H_4	51[c]	-
5	**5e**	*t*-Bu	Cl	*p*-(*t*-Bu)C_6H_4	71[b,c]	3.4/1
6	**5f**	*t*-Bu	H	*p*-(*t*-Bu)C_6H_4	74[b]	4.5/1

[a]Reaction conditions: substrate (0.1 mmol), AgOAc (20 mol%), **L3** (20 mol%), $PhI(OTFA)_2$ (2.0 equiv), K_2CO_3 (2.0 equiv), PhCl/DCE (1.0 mL/1.0 mL), 120 °C, 1 h. [b]Total yield of two isomers. [c]Yield of isolated corresponding alcoholysis products. [d]The ratio of the isomers was determined by ^1H or ^{19}F NMR of the crude reaction mixture.

migration product was afforded in good yield but with a poor selectivity (**6a**/**6a**′ = 1.4/1, entry 1). This result indicated that both phenyl and 4-chlorophenyl worked as migrating groups, but the relatively more electron-rich phenyl group was preferred. When 4-chlorophenyl was replaced by 4-trifluoromethylphenyl, which is considered a stronger electron-deficient substituent (**5b**), a moderate yield was obtained with a better ratio (**6b**/**6b**′ = 5.9/1, entry 2), which might arise from the bigger electronic difference between two substituents. To get more information on the electronic effect, we kept 4-trifluoromethylphenyl and used the more electron-rich 4-methylphenyl (**5c**). A moderate yield with an excellent ratio was obtained (**6c**/**6c**′ = 25/1, entry 3). Predictably, 4-trifluoromethylphenyl and 4-*tert*-butylphenyl (**5d**) gave a sole migration product (**6d**), arising from the best migrating preference of the 4-*tert*-butylphenyl group. Other pairs with 4-*tert*-butylphenyl and either 4-chlorophenyl (**5e**) or phenyl (**5f**) also gave excellent yields (entries 5 and 6). Interestingly, the pair of 4-*tert*-butylphenyl and phenyl gave a slightly better selectivity (**6e**/**6e**′ = 3.4/1, entry 5, vs **6f**/**6f**′ = 4.5/1, entry 6), which could not be explained at this stage. In general, the electron-rich aryl substituents were preferred to give major migration products. The migrating ability of different aryl groups can be summarized as electron-poor aryl < phenyl < electron-rich aryl groups. This conclusion is consistent with the formation of an electron-deficient N-centered radical (or cation) with a very strong electron-withdrawing Tf group, which preferred to attack electron-rich groups to form σ-complex intermediates.

The migration product **2a** could be easily transformed into the corresponding 1,3-hydroxylamine (**7**) when the solution of **2a** was filtering through a thin pad of basic Al_2O_3 (Scheme 4a). **2a** could also be easily converted to tetrahydroquinoline **8** in a

Scheme 4. Alcoholysis and Cyclization of Acyloxylated Amides and Control Experiments



quantitative yield by treating the reaction mixture with concentrated sulfuric acid, providing an alternate way to produce the bioactive tetrahydroquinoline scaffold from the linear amine derivatives,[11] thus extending the potential application of this chemistry.

To get insight on the mechanism, we performed control experiments. When 1.0 or 0.5 equiv of TEMPO was used as a radical scavenger, migration was completely inhibited and only **1a** was recovered (Scheme 4b). However, when 0.2 or 0.1 equiv of TEMPO was used, the migration was only partly inhibited. These results indicated that termination of the migration by TEMPO might not be induced by killing the oxidant while quenching the radical intermediate. In order to further verify our hypothesis, **9** was prepared and tested in the presence of triethylborane and O_2 as a radical initiator (Scheme 4c). Indeed, the migration product (**10**) was obtained with a high yield, accompanied by a small amount of reducing amide. This result proved the feasibility of the radical pathway.

Thus, we proposed the mechanism as shown in Figure 1, although other possibilities could not be ruled out at this stage.

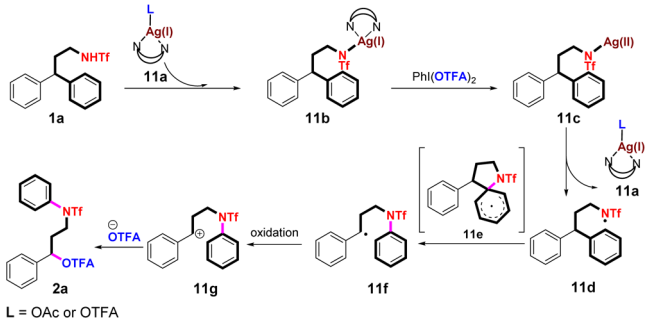


Figure 1. Proposed reaction mechanism.

First of all, **1a** was deprotonated and coordinated to **11a** to form Ag complex **11b**. With support from **L3** and an N anion ligand, the Ag(I) center became very electron rich and was easily oxidized to Ag(II) complex **11c** by $PhI(OTFA)_2$.[12] Subsequently, homolytic cleavage of the N−Ag bond took place to produce the electron-deficient N-centered radical **11d** and regenerate Ag(I) species. Finally, **11d** underwent intramolecular attack on the phenyl ring to form the key intermediate σ-complex **11e** by dearomatization, facilitating the final aryl migration to produce a relatively stable benzylic radical, **11f**.[6a,b] This benzylic radical **11f** could be oxidized to

DOI: 10.1021/jacs.5b10267
J. Am. Chem. Soc. 2015, 137, 14586−14589

the corresponding cation **11g** by presenting oxidants. $TFAO^-$, generated in the previous stage, came back to react with **11g** to give the desired products **2a**. As suggested in Li's development with Ag(III) as potential reactive species,[12b] we also tried **1a** in the presence of $AgNO_3$ and Selectfluor reagent; however, only **1a** was recovered. This result did not support the Ag(III) intermediate in our system.

In summary, we have developed a novel silver-catalyzed long-distance aryl migration of γ,γ-disubstituted triflic amides through C−C bond cleavage, accompanied by the formation of new C−O/C−N bonds. More electron-rich aryl groups showed better performance than electron-deficient aryl motifs during the migration. The migration products were easily converted to γ-hydroxy amines and tetrahydroquinoline derivatives under mild conditions. According to the control experiments, this transformation was proposed to proceed through a silver-promoted radical pathway. Studies to clearly understand the mechanism and explore the potential applications are underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b10267.

Experimental procedures, analytical data, and NMR and XRD spectra of products (PDF)

X-ray crystallographic data for **2a** (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Prof. Wen-Xiong Zhang and Dr. Neng-Dong Wang for their help on the X-ray crystallographic analysis and Prof. Armido Studer for a useful discussion. Financial support by MOST (2015CB856600) and NSFC (Nos. 21332001 and 21431008) is gratefully acknowledged. T.Z. was supported in part by a Postdoctoral Fellowship from Peking-Tsinghua Center for Life Sciences and China Postdoctoral Science Foundation Grant (2014 M550546).

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DOI: 10.1021/jacs.5b10267
J. Am. Chem. Soc. 2015, 137, 14586−14589