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Facile Synthesis of Unsymmetrical Acridines and Phenazines by a Rhodium(III)-Catalyzed Amination, Cyclization and Aromatization Cascade

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Abstract

New formal [3 + 3] annulations have been developed to obtain acridines and phenazines from aromatic azides and aromatic imines and azobenzenes, respectively. These transformations proceed through a cascade process of Rh(III)-catalyzed amination followed by intramolecular electrophilic aromatic substitution and aromatization. Acridines can be directly prepared from aromatic aldehydes by *in situ* imine formation using catalytic benzylamine.

Rh(III)-catalyzed C-H functionalization has proven to be a versatile and highly functional group compatible approach for the synthesis of important classes of heterocycles^{1,2} with additions to alkynes,³ alkenes,⁴ allenes,⁵ aldehydes,⁶ imines,^{6c} carbon monoxide,⁷ isonitriles,⁸ isocyanates⁹ and diazo compounds¹⁰ all having been utilized. Capitalizing on recent reports of Rh(III)-catalyzed C-H functionalization with aromatic and sulfonyl azide coupling partners,^{11a–c,12,13} Glorius has very recently described a novel Rh/Cu-cocatalyzed synthesis of *1H*-indazoles through C-H amidation of benzimidates with sulfonyl azides followed by oxidative N-N bond formation.^{11d} Herein, we report new formal [3 + 3] annulations to prepare acridines and phenazines by Rh(III)-catalyzed C-H amination with aromatic azides followed by *in situ* intramolecular electrophilic aromatic substitution and aromatization (Figure 1). Despite the prevalence of acridines and phenazines in natural products, pharmaceuticals and materials,^{14,15} as exemplified by photosensitizers or photocatalysts, the regioselective preparation of derivatives with substitution on both rings can be challenging.^{16,17} In contrast, the approach reported here provides very rapid access to unsymmetrical derivatives with precise placement of diverse functionality at almost all positions about the acridine and phenazine cores.

We initiated our investigation by exploring the Rh(III)-catalyzed addition of the imine of benzaldehyde **1a** to phenyl azide **2a** (see Supporting Information for optimization table). The use of 10 mol % of the convenient pre-formed cationic rhodium catalyst [Cp^{*}Rh(CH₃CN)₃(SbF₆)₂] in dichloroethane (DCE) was found to optimal, providing the product **3a** in 57% yield (eq 1). Because the aniline released upon cyclization and aromatization might interact with the catalyst, CF₃CO₂CH₂CF₃ or acetic anhydride were

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Supporting Information

Complete experimental procedures, spectral data for new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

investigated as scavengers of this byproduct. Both additives resulted in a significant increase in yield to 71% and 77%, respectively.

Having defined an effective catalyst and reaction conditions for the synthesis of acridine **3a** from pre-formed imine **1a**, we next explored the possibility of conducting the reaction directly from aldehydes in the presence of a catalytic amount of an amine. This approach would enhance the utility of the method because a vast number of aldehydes are commercially available thus providing rapid entry to a wide range of acridines. The proposed cascade sequence would require *in situ* condensation of an aldehyde and an amine to form an imine necessary to direct C-H amination followed by cyclization to generate the acridine with release of the amine for another catalytic cycle. Although we had previously found that released aniline is detrimental to the reaction, we reasoned that if catalytic amounts of amine were used, it might be sequestered as the imine until the reaction neared completion.

(1)

The importance of the imine directing group was first demonstrated by attempting to directly couple aldehyde **4a**, which resulted in only trace amount of product (entry 1, Table 1). Addition of 10 mol % of aniline provided product **3a** in 15% yield (entry 2), and including MgSO₄ as drying agent along with 10 mol % and 20 mol % of aniline further increased the yield to 26% and 40%, respectively (entries 3 and 4). While anilines substituted with either electron-rich or -deficient groups failed to further improve the yield (entries 5 and 6), benzylamine resulted in a slightly higher yield (entry 7). Moreover, by doubling the benzylamine loading, a further improvement to 65% was observed (entry 8). The branched and more sterically hindered cyclohexylamine was not as effective (entry 9). However, diluting the reaction mixture two-fold significantly enhanced the yield to 76% (entry 10), which is comparable to the yield observed in the reaction with pre-formed imine (see eq 1). Although catalytic *in situ* imine formation has been utilized for Rh(I) catalysis,¹⁸ to the best of our knowledge, this is the first example of using catalytic *in situ* imine formation for Rh(III)-catalyzed C-H functionalization.

Substrate scope was explored with a diverse set of aromatic aldehydes and aromatic azides (Table 2). The reaction shows excellent functional group compatibility and provided acridines **3** in good yields for aldehydes substituted with chloro (**3b**), iodo (**3c**), fluoro (**3g**), ester (**3d, k-o**), methoxy (**3e**), indole (**3i**) and acetamide (**3f**) groups and aromatic azides substituted with trifluoromethyl (**3k**), chloro (**3l**), methoxy (**3m**) and alkyl (**3n, o**) functional groups. Moreover, thiophene could also be incorporated (**3j**). While both electron-neutral and -rich aromatic aldehydes are suitable for this transformation, electron-poor aldehydes afforded the products in higher yields (**3d** versus **3e-f** and **3i**, respectively). Aromatic aldehydes with ortho- (**3g**), meta- (**3h**) and para- (**3b-f, k-o**) substitution were all compatible, with the meta-methyl substituted benzaldehyde exclusively providing product **3h** resulting from C-H activation at the less hindered site. Interestingly, the yields obtained in this transformation are not sensitive to the electronic or steric effects introduced by substitution on the aromatic azide. Substitution with electron-donating (**3j, 3m-o**), -neutral (**3b-i**), or -

withdrawing (**3k,l**) groups and at ortho- (**3n**), meta- (**3o**), or para- (**3k-m**) positions all provided good to excellent yields. However, in contrast to the complete regioselectivity observed for cyclization of a meta-substituted aromatic aldehyde input (see **3h**), meta-methyl substitution on the phenyl azide proceeded with good but not absolute regioselectivity favoring cyclization at the least hindered site (**3o**). Heterocycles on both aldehyde (**3i**) and azide (**3j**) are well tolerated and provide the products in moderate to good yields.

The possibility of extending substrate scope to ketones, which would lead to acridines with substitution at the 9-position, was next investigated. Ketones are much less efficiently converted to imines than aldehydes, and consequently the protocol for *in situ* formation of the imine using a catalytic amount of amine resulted in less than 10% of product, not only for MgSO₄ and molecular sieves, but also for more powerful water scavengers and Lewis acid additives such as Ti(*i*-OPr)₄. We therefore turned our attention to the use of pre-formed imines under the conditions optimized for coupling pre-formed aldimines with azides (see eq 1). Under these conditions the ketimine-derived 9-substituted acridines were obtained in good to excellent yields (Table 3). Both electron deficient (**6b**) and sterically hindered (**6c**) substituents could be installed at the central position of the acridine ring. In analogy to the steric and electronic effects observed for the reactions with aldehydes, electron-donating groups (**6e**) provided the product in lower yields relative to electron-withdrawing (**6d, 6j**) and electron-neutral groups (**6f**). Moreover, meta-substitution selectively generated the product as a single isomer with amination at the least hindered site (**6f**). In contrast to the high yields observed for the reaction with an ortho-substituted benzaldehyde (see **3g**, Table 2), ortho-substitution on the ketimine resulted in a modest yield (**6g**), although ortho-substitution on the aromatic azide provided the product **6i** in high yield. Electron-deficient phenyl azides (**6k**) provided the product in a moderate yield as compared to the very good yields observed for electron-rich (**6j**) and neutral azides (**6a-f**). Heterocyclic azides as exemplified by an azidothiophene afforded the product **6h** in high yield.

Having established broad scope in the synthesis of acridines with or without substitution at the central 9-position, we next considered the possibility of extending this formal [3+3] annulation approach to the synthesis of phenazines **8** from azobenzenes **7** (Table 4). The conditions previously optimized for ketimines provided product **8a** in low yield whether or not acetic anhydride was used as an additive (entries 1 and 2). Glacial acetic acid was evaluated as solvent because we envisioned that it might facilitate cyclization as well as sequester the released aniline by hydrogen bonding or salt formation (entry 3). Encouraged by the considerable improvement in yield, alternative counterions were next explored. While use of (Cp**Rh*Cl₂)₂ and AgSbF₆ resulted in a yield comparable to that observed with the corresponding pre-formed catalyst (entry 4), use of the completely non-coordinating counterion B(C₆F₅)₄ resulted in a significant improvement providing phenazine (**8a**) in 67% yield (entry 5). A comparable yield was also obtained when unsymmetrical azobenzene **7** (R = CH₃) was used (entry 6). For this substrate the reaction exclusively occurs on the ring lacking 3,5-disubstitution consistent with the strong steric bias against Rh-(III) selective C-H functionalization adjacent to a meta-substituent.^{6a}

Reaction scope was evaluated by the preparation of unsymmetrical bis-substituted derivatives for which the regioselective placement of functionality can be challenging using alternative methods (Table 5).¹⁷ Unsymmetrical azobenzenes with 3,5-dimethylaniline acting as a directing group were employed because this type of azobenzene can readily be prepared by simple condensation between commercially available anilines and 3,5-dimethylnitrosobenzene. Consistent with acridine synthesis, good functional group compatibility was observed with bromo (**8b**), chloro (**8i**), fluoro (**8f**), trifluoromethyl (**8c**), methoxy (**8d**), keto (**8b-g**) and ester (**8a, 8h-k**) substituted products all being produced.

Azobenzenes with diverse electronic properties proved to be effective substrates, although electron-donating groups (**8d**) provided significantly lower yields relative to electron-withdrawing (**8c**, **8f**, and **8g-k**) and electron-neutral groups (**8a**, **8b** and **8e**). Substitution at the ortho- (**8f**), meta- (**8e**), and para- (**8b-d**, **8g-k**) positions were all tolerated, with meta-methyl substitution producing a single isomer with amination at the least hindered site (**8e**). Both electron deficient (**8a-h**) and electron neutral (**8j** and **8k**) azides were effective coupling partners, and ortho-substitution was not at all detrimental to the reaction yield (**8k**).

The proposed mechanistic pathway for this cascade reaction is shown in Scheme 1. Imines or azobenzenes **9** undergo ortho-directed C-H bond activation to give metallacycles **10**¹⁹ followed by coordination and migratory insertion with azides to afford metallacycle **12**. This sequence of reactions corresponds to mechanisms previously proposed for other Rh(III)-catalyzed reactions with organic azides^{11a-c} and is also consistent with the lack of reactivity of the aromatic azide with the Rh(III)-catalyst unless the azobenzene or imine substrate is present. Protonation of metallacycle **12** then releases diarylamine **13** and the Rh(III) catalyst. Under the reaction conditions, diarylamine **13** undergoes intramolecular electrophilic aromatic substitution to **14** followed by aromatization to give the desired acridines and phenazines **15**. Under standard conditions **13** does not accumulate even for the coupling of electron deficient aryl azide **2b** with azobenzene **7b**. However, when these coupling partners were reacted at 90 °C for 7 h, trace intermediate **13** and approximately 10% of phenazine **8a** were detected by ¹H NMR and LC-MS. Upon repeating the reaction on larger scale, chromatography resulted in the isolation of 86% of the azobenzene starting material **7** along with 9% of product **8a** and approximately 1% of the uncyclized diarylamine **13**.

In summary, formal [3+3] annulations of aromatic azides with imines to give acridines and with azobenzenes to give phenazines have been developed. These transformations proceed by Rh(III)-catalyzed ortho-C-H amination followed by intramolecular electrophilic aromatic substitution and aromatization. A broad range of acridines and phenazines can be generated with precise placement of diverse functionality, including for unsymmetrical disubstituted derivatives. Moreover, through the use of catalytic benzylamine to generate the requisite imine *in situ*, aromatic aldehydes can be used to rapidly and directly access acridines lacking substitution at the 9-position.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Previous Work: Indazole synthesis using sulfonyl azides **This Work: Acridine and phenazine synthesis with aryl azides**

Figure 1.
Heterocycles by tandem C-H amination and cyclization.

Scheme 1.
Proposed Cascade Mechanism

Table 1

In situ Imine Formation with Catalytic Amine^a

entry	R	amine loading (mol %)	additive	4a Conc. [M]	yield (%) ^b
1	--	--	--	0.10	<3
2	Ph	10	--	0.10	15
3	Ph	10	MgSO ₄	0.10	26
4	Ph	20	MgSO ₄	0.10	40
5	<i>p</i> -OMePh	20	MgSO ₄	0.10	33
6	<i>p</i> -CF ₃ Ph	20	MgSO ₄	0.10	24
7	Benzyl	20	MgSO ₄	0.10	49
8	Benzyl	40	MgSO ₄	0.10	65
9	Cyclohexyl	40	MgSO ₄	0.10	50
10	Benzyl	40	MgSO ₄	0.05	76 (76) ^c

^a Conditions: **4a** (0.10 mmol), **2a** (0.15 mmol) in 1.0 or 2.0 mL of solvent for 20 h.

^b Determined by ¹H NMR relative to 2,6-dimethoxytoluene as an external standard.

^c Isolated yield at 0.20 mmol scale of **4a**.

Table 2

Substrate Scope for Acridine Synthesis with Aldehydes^{a,b} ^a Conditions: aldehyde (0.20 mmol), azide (0.30 mmol), 100 mg of MgSO_4 in 4.0 mL of DCE for 20 h.^b Isolated yield.^c Combined yield with other minor isomer having methyl substituted at 8-position in 7:1 ratio.

Table 3

Substrate Scope for Acridine Synthesis with Ketone-derived imines^{a,b} ^aConditions: imine (0.20 mmol), azide (0.30 mmol), Ac_2O (0.40 mmol) in 2.0 mL of DCE for 20 h.^bIsolated yield.

Table 4

Optimization of Phenazine Synthesis^a

entry	R	Rh(III) source	additive	solvent	yield (%) ^b
1	H	Cp*Rh(CH ₃ CN) ₃ (SbF ₆) ₂	--	DCE	17
2	H	Cp*Rh(CH ₃ CN) ₃ (SbF ₆) ₂	Ac ₂ O	DCE	3
3	H	Cp*Rh(CH ₃ CN) ₃ (SbF ₆) ₂	--	AcOH	48
4	H	(Cp*RhCl ₂) ₂	AgSbF ₆	AcOH	43
5	H	(Cp*RhCl ₂) ₂	AgB(C ₆ F ₅) ₄	AcOH	67 (61) ^c
6	CH ₃	(Cp*RhCl ₂) ₂	AgB(C ₆ F ₅) ₄	AcOH	63

^a Conditions: **7** (0.10 mmol), **2a** (0.15 mmol) in 2.0 mL of solvent 24 h.^b Determined by ¹H NMR relative to 2,6-dimethoxytoluene as an external standard.^c Isolated yield at 0.20 mol scale of **7a**.

Table 5

Substrate Scope for Phenazine Synthesis^{a,b} ^a Conditions: azobenzene (0.20 mmol), azide (0.30 mmol) in 4.0 mL of HOAc for 24 h.^b Isolated yield.^c 8:1 ratio with the other separable minor isomer having methyl substituted at 6-position.