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Intramolecular azavinyl carbene-triggered rearrangement of furans†

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An intramolecular rhodium-catalyzed reaction of 1-tosyl-1,2,3-triazoles with furans has been explored. The tosylimino functionality was found to play a significant chemical role participating in the subsequent domino-transformations of a key reaction intermediate. One of the reaction pathways leads to valuable 2-formyl- and 2-acetylpyridine building blocks, which could be obtained in *one-pot* starting from easily accessible (furan-2-ylmethyl)propargyl amines. An original method for the synthesis of highly functionalized indolizines from the obtained pyridines has been proposed.

Introduction

Ten years ago Gevorgyan and Fokin realized the colossal synthetic potential of metal-intercepted α -diazoimine tautomers¹ of sulfonyl triazoles,² which were easily accessed through copper-catalyzed azide-alkyne cycloaddition (CuAAC).³ The resulting α -iminocarbene species possess the characteristic reactivity of carbenes generated by denitrogenative decomposition of conventional diazo compounds; specifically, they undergo cheletropic reactions, X-H and C-X insertions, ylide formation or rearrangements (Fig. 1).⁴ However, the sulfonyl

imine functionality exhibits untypical nucleophilicity, which allows the azavinyl carbenoids to undergo transannulations following the addition of a nucleophile to the carbene centre.⁵ Eventually, such an upgraded reactivity of rhodium transient azavinyl carbenoid species affords a high level of synthetic flexibility that is to some extent controlled by the nature of a reaction partner.

Furans represent nontrivial biomass-derived building-blocks⁶ known for their propensity to undergo dearomatization^{7,8} forming diverse carbo-⁹ and heterocyclic¹⁰ compounds under electrophilic conditions.

Understandably, furans were tested as nucleophiles in a reaction with carbenes derived from diazo compounds. While intermolecular reactions usually result in the formation of cyclopropane and dienone mixtures with poor regiocontrol,¹¹ intramolecular processes afford better chemoselectivity. In particular, the denitrogenative decomposition of various (furan-2-yl)-tethered diazo compounds usually proceeds through the same spiro-intermediate,^{12,13} and yet leads to products with limited synthetic utility (Fig. 2a). In turn, decomposition of (furan-2-yl)-tethered 1-sulfonyl-1,2,3-triazoles would result in the formation of a common spiro-key intermediate that could be intercepted by an imino group, leading to compounds of type **A** (Fig. 2b, path I). Alternatively, the key intermediate might rearrange to azatriene **B** that could further be converted to a variety of nitrogen-containing heterocycles (Fig. 2b, path II). In either scenario there is the possibility for rapid accessing the molecular complexity from rather structurally simple starting materials.

To our surprise, we could not find any reports on intermolecular rearrangements of furans initiated by iminocarbene species derived from triazoles, although examples of denitrogenative decomposition of triazoles in the presence of a furanyl substituent within the same molecule are known.^{14,15} In order to fill the methodological gap, we sought to explore the synthetic prospects of the aforementioned transformation. Very

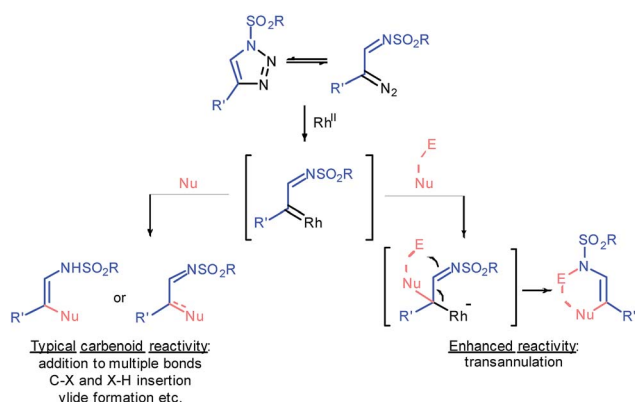


Fig. 1 General reactivity patterns of 1-sulfonyl-1,2,3-triazoles.

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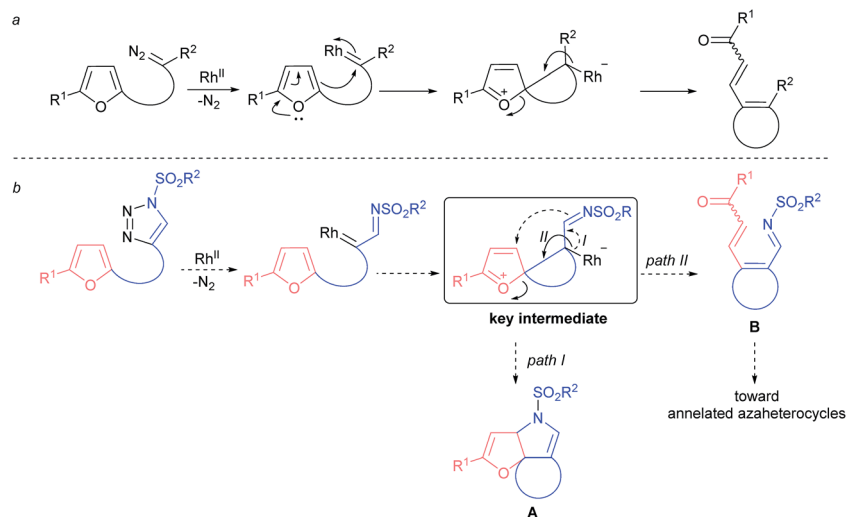


Fig. 2 Intramolecular rhodium carbenoid-triggered ring-opening of furans: (a) known reactivity; (b) concept for this work.

recently, Hashmi *et al.* described a synthetic method toward functionalized pyrroles based on the rearrangement of a furan ring in the gold(III)-catalyzed reaction of propargylfurfuryl amines with anthranils.¹⁶ The reaction is believed to proceed through the intermediate formation of gold-stabilized imino-carbene species that attack the furan system followed by its dearomatization. The denitrogenative decomposition of furyl-tethered triazoles, in contrast, would provide regioisomeric iminocarbenes, which upon reaction with a furan ring could lead to the formation of valuable products of different architectures. Herein, we report our initial studies of intramolecular azavinyl carbene-triggered rearrangement of furans.

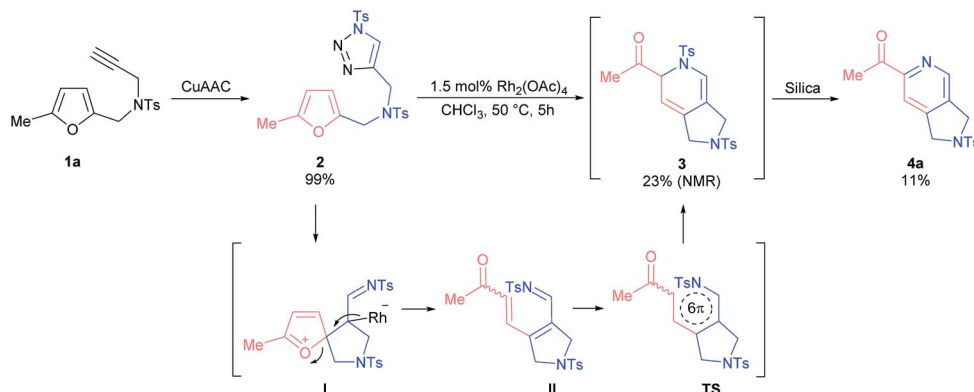
Results and discussion

Our exploratory studies commenced with triazole **2** as a model substrate, which was obtained *via* CuAAC from propargyl amine **1a** (Scheme 1). Treatment of triazole **2** with rhodium acetate dimer in chloroform at 50 °C led to a full conversion of the starting material within 5 h. Careful analysis of the crude reaction mixture revealed that the main component among the formed products appeared to be dihydropyridine **3**. However, all

attempts to isolate compound **3** by column chromatography on silica gel failed; the only product detected was 2-acetylpyridine **4a**. The same outcome was observed when the reaction mixture was treated with a base. Apparently, the formation of 2-acetylpyridine **4a** resulted from 6 π -azaelectrocyclization¹⁷ of initially formed dihydropyridine **II** followed by aromatization through elimination of sulfinate.¹⁸ Stimulated by the high synthetic value of 2-acetylpyridines as intermediates in medicinal¹⁹ and material²⁰ chemistry, we decided to study the discovered transformation in more detail.

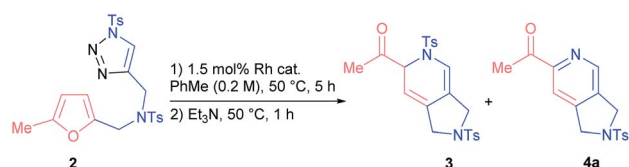
The optimization of reaction conditions revealed that toluene was the solvent of choice for the formation of dihydropyridine **3a** (Table 1, entry 1; for more details, see the ESI†). Further screening of rhodium(II) sources led us to identify Rh₂(OOct)₄ as the optimal catalyst for the first cascade transformation (entries 2–5). As compound **3** appeared to be quite unstable, we continued tuning the reaction conditions towards final acetylpyridine **4a** in a *one-pot* mode.

After some experiments, we found that addition of two equivalents of Et₃N resulted in the clean transformation of dihydropyridine **3a** into its unsaturated derivative **4a** (entry 8).



Scheme 1 Initial results.



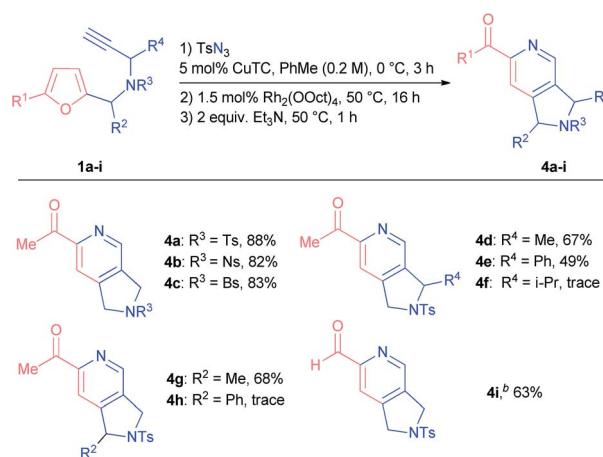
Table 1 Optimization of the reaction conditions^a


Entry	Rh cat.	Et ₃ N (equiv.)	Yield of 3 ^b , %	Yield of 4a ^b , %
1	Rh ₂ (OAc) ₄	—	55	Trace
2	Rh ₂ (OCOTr) ₄	—	62	Trace
3	Rh ₂ (OPiv) ₄	—	63	Trace
4	Rh ₂ (OHex) ₄	—	75	Trace
5	Rh ₂ (OOct) ₄	—	90 ^c	Trace
6	Rh ₂ (OOct) ₄	(1)	Trace	79 ^c
7	Rh₂(OOct)₄	(2)	Trace	93^c (90)^d

^a General considerations: reactions were performed on a 0.05 mmol scale of **2** under dinitrogen; freshly distilled and degassed toluene and Et₃N were used. ^b NMR yields with CH₂Br₂ as an internal standard. ^c Reaction time – 10 h. ^d Reaction was performed on a 0.5 mmol scale; yield of the isolated product is given in parentheses; reaction time for the first step – 16 h.

With the aim of establishing a convenient synthetic method towards 2-acylpyridines, we integrated the CuAAC step into a single *one-pot* protocol starting from propargyl amines **1**. To our delight, the addition of an extra step had almost no effect on the outcome of the model reaction; the yield of pyridine **4a** was 88% (Scheme 2). Moreover, on a gram-scale the method afforded pyridine **4a** in comparable yield with the use of only 0.5 mol% of rhodium catalyst (see the ESI† for details).

Following the optimization studies, we sought to study the influence of various substituents at different positions of the starting material on the reaction outcome. Substituted propargyl amines **1a–i** were screened first (Table 2). Bromo and nitro substituents in other tested sulfonyl protection groups were tolerated well under the optimized conditions (compounds **4b** and **c**). It was possible to introduce substituents at propargylic (compounds **4d** and **e**) and furfuryl positions (compound **4g**) of the starting material, although the overall transformation resulted in lower yields of the respective products, probably due to steric reasons. Indeed, more bulky substituents at either position prevented the furan from being attacked by a carbene centre in an initial step: in the cases of starting materials **1f** and **1h** we observed the formation of corresponding triazoles that decomposed over time. After additional tuning of reaction

Table 2 Scope of furfuryl amines^a

^a General considerations: reactions were performed on a 0.5 mmol scale of propargyl amines **1** under dinitrogen; stepwise addition of catalysts and reagents. For more details, see the ESI. ^b Second step – 1 h at 75 °C and then third step – 1 h at 75 °C.

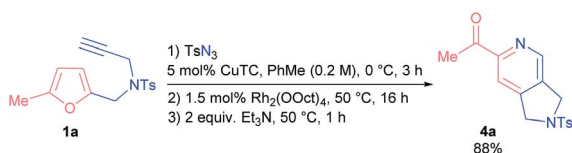
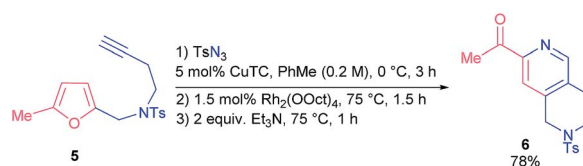
parameters, we were also able to obtain 2-formylpyridine **4i** in 63% yield.

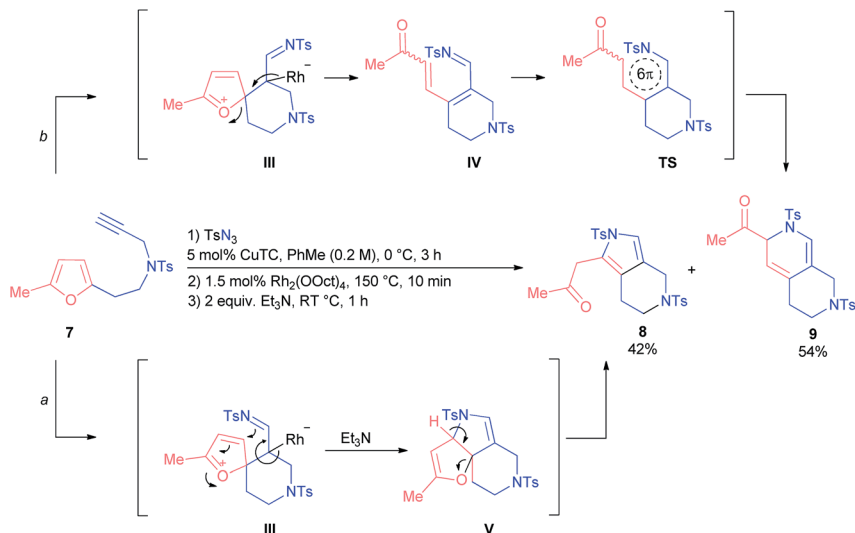
Next, we studied substrates with an extended tether that linked the triazole fragment and a furan ring. Thus, homopropargylamine **5** reacted smoothly under slightly altered reaction conditions to provide tetrahydronaphthiridine **6** (78%) (Scheme 3).

When we tested homofurfurylamine **7**, which was forced to react under quite harsh conditions, we observed the formation of pyrrole **8** as well as dihydropyridine **9** (Scheme 4). Presumably, pyrrole **8** was the product of an alternative reaction where initially formed spiro-intermediate **III** was trapped intermolecularly with the imino group followed by base-induced ring-opening of dihydrofuran intermediate **V** (route a). In turn, dihydropyridine **9** was formed *via* 6π-azaelectrocyclization of azatriene **IV** following the ring-opening of initial intermediate **III** (route b). Evidently, the nature of the tether modulates the geometry of an intermediate **III** at such an elevated reaction temperature, so that it can demonstrate alternative reactivity.

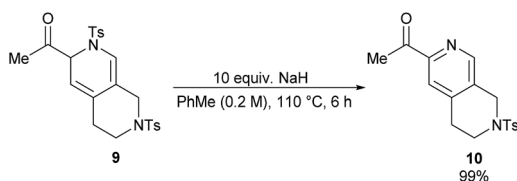
Dihydropyridine **9** was found to be more stable than its analogue, dihydropyridine **3**. Conversion of compound **9** into the corresponding pyridine **10** required much harsher reaction conditions as well (Scheme 5).

We examined the reactivity of propargyl ethers **11** that were found to be more reactive than related amines **1** (Table 3).

Scheme 2 One-pot synthesis of pyridine **4a**.Scheme 3 Synthesis of tetrahydronaphthiridine **6**.



Scheme 4 Divergent reactivity of homofurfurylamine 7.



Scheme 5 Synthesis of tetrahydronaphthiridine 10.

Consequently, they had to be converted under milder conditions in order to avoid undesired side reactions.

Generally, substrates **11** afforded corresponding products **12** in higher yields, even those bearing bulky substituents in the furfuryl position (products **12c** and **d**). Noteworthy, 2-formylpyridine **12e** was as well obtained in practical yield.

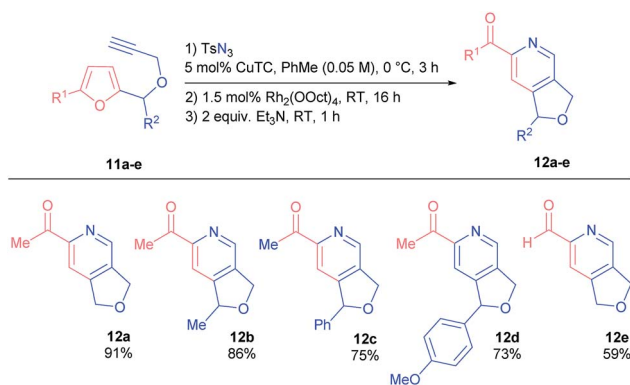
The reaction of propargyl ethers with voluminous substituents at C(5) of a furan ring (compounds **11f** and **g**) stopped at

the formation of *Z*-azatrienes **13a** and **b**, the products of the ring-opening of the initial spiro-intermediates (Scheme 6). Likely, bulky groups obstruct the electrocyclicization of the respective azatrienes. All attempts to force the reactions only led to *Z*-to-*E* isomerization of the α,β -unsaturated ketone moiety.

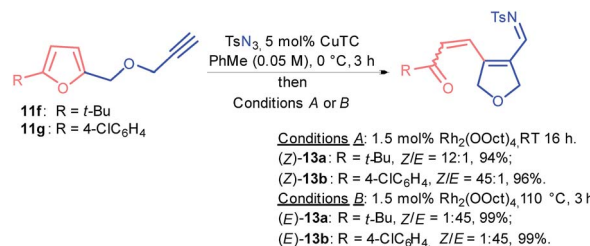
Finally, we probed propargyl ester **14** with a lengthened linker. Under various conditions the only product we always detected was the very unstable enol ether **15**, which, apparently, was formed through 1,2-shift of a hydride to a carbene atom. Eventually, we found conditions that provided a nearly quantitative yield of compound **15** (Scheme 7).

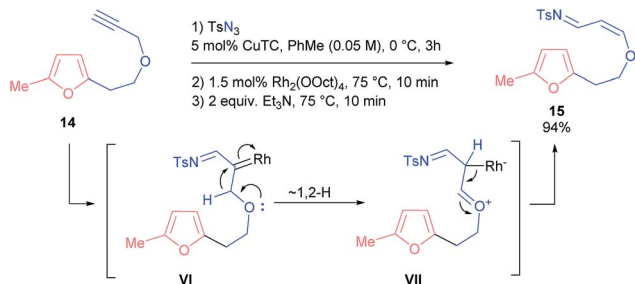
It is known that 1,2-hydride shifts often follow the denitrogenative decomposition of 4-alkyltriazoles, which reduces the yields of the target compounds.²¹ Possibly, this competing reaction also affects the outcome of the studied processes. It seems that the observed sigmatropic rearrangement is a kinetically controlled reaction in the case of substrate **14**: both the longer tether and higher proclivity of the oxygen atom to donate its electron pair (compared to the NTs group) make enol **15** a predominant product.

2-Acylpyridines are known to be largely used for the synthesis²² of indolizines, indolizidines and their close structural analogues, which represent core frameworks for the vast number of alkaloids and biologically active compounds.²³ We attempted to further extend the application of the obtained

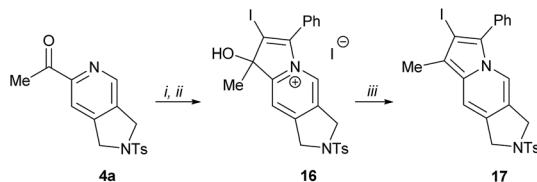
Table 3 Scope of furfuryl ethers^a

^a General considerations: reactions were performed on a 0.5 mmol scale of a propargyl ether **11** under dinitrogen; stepwise addition of catalysts and reagents. For more details, see the ESI.

Scheme 6 Reactivity of propargyl ethers **11f** and **g**.



Scheme 7 Reaction of propargyl ether 15.



Scheme 8 Synthesis of indolizine 17. Reaction conditions: (i) 1.5 equiv. (phenylethynyl)lithium, 3 equiv. LiBr, Et₂O/PhH, RT, and 15 h; (ii) 1.5 equiv. I₂, DCM, RT, and 5 h (93% over 2 steps); (iii) 2 equiv. NaBH₄, MeOH, RT, and 30 min (99%).

products for the synthesis of functionalized indolizines through trivial functional group manipulations. The addition of (phenylethynyl)lithium to a carbonyl group of 2-acetylpyridine **4a** followed by treatment of the resulting propargyl alcohol with molecular iodine afforded indolizinium salt **16** in excellent yield (Scheme 8). The reduction of compound **16** with sodium borohydride directly led to 2-iodoindolizine **17** through the simultaneous dehydration of intermediate dihydroindolizinol. To the best of our knowledge, this synthetic pathway has not been reported previously.

Conclusions

In conclusion, we studied some aspects of previously non-reported intramolecular reactions of azavinyl rhodium carbenoid species with furans. Our findings enabled us to develop a straightforward *one-pot* protocol toward fused 2-acetyl- and 2-formylpyridines from easily accessible biomass-derived furan building-blocks. We demonstrated that the obtained pyridines could be utilized for the synthesis of highly functionalized indolizines through the original high-yielding protocol. Additionally, we found that rearrangement of furans triggered by rhodium iminocarbenes could possibly proceed *via* two distinct pathways, thereby providing different heterocyclic frameworks. Our initial results highlight that intermolecular rearrangement of furyl triazoles has high potential as a practical tool for the design of various heterocyclic compounds. Further aspects of the discovered transformations will be reported in due course.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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