OL | Organic Letters

pubs.acs.org/OrgLett Letter

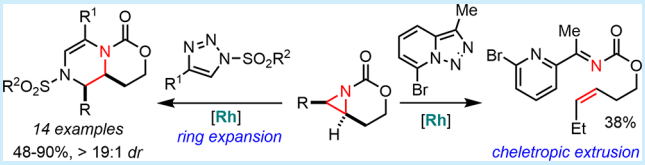
Rh-Catalyzed Aziridine Ring Expansions to Dehydropiperazines

Hillary J. Dequina,[§] Josephine Eshon,[§] William T. Raskopf, Israel Fernández,* and Jennifer M. Schomaker*

Cite This: https://dx.doi.org/10.1021/acs.orglett.0c01124 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Piperazines are prevalent in pharmaceuticals and natural products, but traditional methods do not typically introduce stereochemical complexity into the ring. To expand access to these scaffolds, we report Rh-catalyzed ring expansions of aziridines and *N*-sulfonyl-1,2,3-triazoles to furnish dehydropiperazines with excellent diastereocontrol. Productive ring expansion proceeds via a pseudo-1,4-sigmatropic rearrangement of an aziridinium ylide species. However, the structural features of the carbene precursor are important, as pyridotriazoles undergo competing cheletropic extrusion to furnish ketimines.



Ylides are unique molecules with a negatively charged carbon atom directly attached to a positively charged heteroatom.[1,2] The first example, a phosphorus ylide, was reported in 1894 (Figure 1A);[3] however, their full synthetic utility was not recognized until 1953, when Wittig utilized them to prepare alkenes from aldehydes and ketones.[4−6] Since then, phosphorus ylide chemistry has provided powerful tools to construct C−C and C−heteroatom bonds.[7,8] Sulfur ylides are popular for the synthesis of cyclopropanes, epoxides, and aziridines.[9−11] Other Group 5 and 6 ylides based on O,[11] As,[12] Se,[10b,13] and Te[10,13] are known; however, these are less synthetically useful.

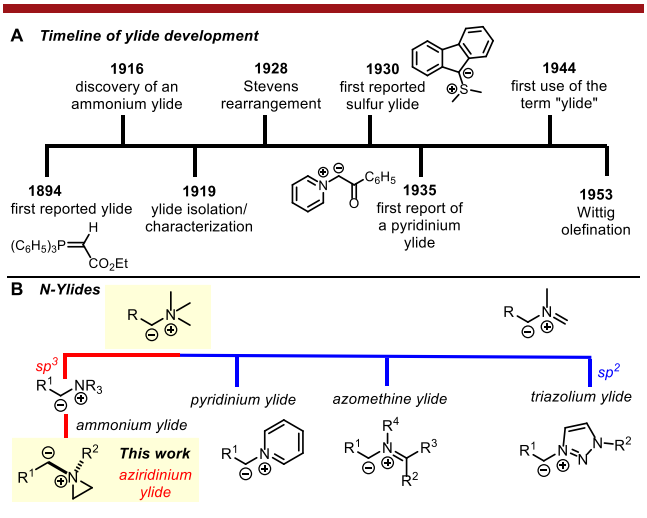


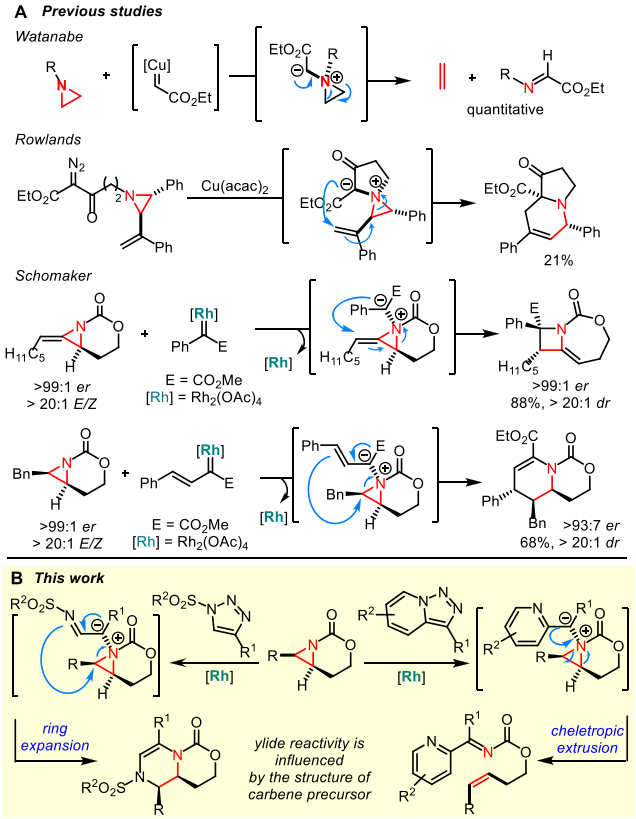
Figure 1. Ylide development and types of N-ylides.

The importance of nitrogen in bioactive molecules has stimulated significant interest in the chemistry of nitrogen ylides. N-Ylides are typically less stable than their S- and P-ylide counterparts and are generated in situ; however, they display an array of interesting reactivities. Common N-ylides (Figure 1B) include ammonium,[1,11] azomethine,[14] pyridinium,[15] and triazolium ylides.[16] While ammonium ylides have been widely employed, versions generated specifically from aziridines, termed "aziridinium ylides", are underexplored. Aziridinium ylides are conveniently generated from the reaction of aziridines with metal-supported carbenes; the potential to harness the reactivity of these intermediates to furnish diverse N-heterocycle scaffolds inspired the studies described in this communication.

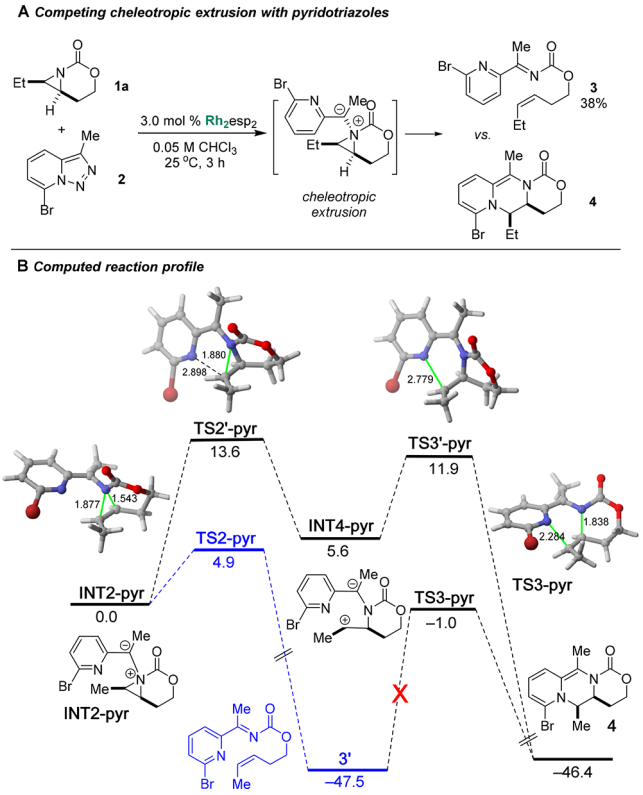
One reason aziridinium ylides have not been extensively investigated is the difficulty in controlling the ultimate fate of the intermediate. In 1972, Watanabe attempted to convert an aziridinium ylide to an azetidine via Cu-catalyzed addition of an electron-rich aziridine to a diazoester.[17] Instead of ring expansion, ethylene and an α-imino ester were observed, suggesting cheletropic extrusion competes (Scheme 1A).[18] In 2004, Rowlands suppressed cheletropic extrusion in favor of a [2,3]-Stevens rearrangement of an aziridinium ylide generated by adding a vinyl aziridine to a Cu-supported carbene (Scheme 1A); however, a competing [1,5]-H shift resulted in only a 21% yield of the heterocycle.[19] In 2017, we reported aziridinium ylides generated from strained aziridines, and Rh-supported carbenes undergo concerted [2,3]-Stevens rearrangement to give methyleneazetidines in good yields and dr with broad scope.[20,21] More recently, we also reported an intermolecular carbene transfer between Rh-bound vinyl

Received: March 30, 2020

Scheme 1. Divergent Reactivities of Aziridinium Ylides



Scheme 2. Cheletropic Extrusion with Pyridotriazole 2[a]



[a]Computed reaction profile with relative free energies (ΔG, computed at 298.15 K and 1 M) and bond distances in kcal/mol and Å, respectively. All data are computed at the SMD-B3LYP-D3/def2-SVP level.

carbenes and aziridines via a pseudo-[1,4]-sigmatropic rearrangement to furnish dehydropiperidines in excellent yields and dr.[22]

Inspired by the lack of structural diversity in piperazines and related heterocycles generated from known methods, we first attempted to prepare fused piperazines. Pyridotriazole **2** (Scheme 2A) is known to form α-imino Rh-supported carbenes upon heating;[23] unfortunately, reaction between **1a** and **2** gave ketimine **3** instead of the desired **4**. The preference for the formation of **3** over **4** was computationally explored (Scheme 2B). Focus was placed on the fate of the metal-free ylide **INT2-pyr**, formed upon nucleophilic addition of the aziridine to the dirhodium carbene, followed by dissociation of the Rh_2 catalyst. Ylide **INT2-pyr** can evolve into alkene **3′** (the Et group in **3** was replaced by a Me in the calculations) via **TS2-pyr** in a highly exergonic transformation (ΔG_R = −47.5 kcal/mol). This saddle point resembles that located for the cheletropic extrusion pathway involving ylide **TS2** (Figure 2, *vide infra*) and is associated with the concerted rupture of both aziridine C−N bonds. Interestingly, calculations indicate that the subsequent aza-Diels−Alder reaction is unfeasible in view of the high barrier computed for this cycloaddition ($\Delta G^{\ddagger}$ > 45 kcal/mol). This can be mainly ascribed to the loss of aromaticity of the pyridine moiety, which is also reflected in the computed endergonicity of the process (ΔG_R = +1.1 kcal/mol), despite the formation of two new C−N bonds.

An alternative sigmatropic rearrangement pathway involving NMs-ylide **INT2-pyr** was located. Instead of a direct pathway leading to **3′**, computations showed a stepwise process which first transforms **INT2-pyr** into the zwitterion **INT4-pyr** (via **TS2′-pyr**), followed by a ring-closure reaction (through **TS3′-pyr**). From the data in Scheme 2B, it is apparent that this alternative pathway is not competitive due to the higher barrier required to reach **TS2′-pyr** (and **TS3′-pyr**), as compared to the chelotropic extrusion pathway via **TS2-pyr**.

Interestingly, the barrier computed for **INT2-pyr** →**TS2′-pyr** is much higher than that computed for the analogous process involving **INT2** (Figure 2, *vide infra*), which can be, at least in part, ascribed to the loss of aromaticity of the pyridine ring. This is supported by markedly different C···N bond distances in the corresponding transition states **TS2′** (Figure 2) and **TS2′-pyr**. While in the former saddle point the computed C···N distance is 2.741 Å, a much longer distance of 2.898 Å is computed in the latter species. This indicates **TS2′-pyr** does not benefit from a significant C···N interaction, although **TS2′** does. As a result, the **INT2-pyr** → **TS2′-pyr** reaction not only is kinetically less favored but also proceeds in a stepwise fashion.

We hypothesized the use of *N*-sulfonyl-1,2,3-triazoles might alter the ultimate fate of the aziridinium ylide, as the nucleophilicity of the α-imino group of metallocarbenes derived from these precursors could bias the reaction toward ring expansion (Scheme 1B). Differences in the electrophilicities of Rh-supported carbenes formed from *N*-sulfonyl-1,2,3-triazoles vs pyridotriazoles, as well as varying steric congestion and ability of the ylide to delocalize charge, could also play roles in dictating the outcome. In addition, the requirement for slow addition of typical diazoesters might be overcome by the use of more robust *N*-sulfonyl-1,2,3-triazole carbene precursors. Ideally, an intermediate α-imino rhodium carbene would be generated, followed by nucleophilic addition

https://dx.doi.org/10.1021/acs.orglett.0c01124
Org. Lett. XXXX, XXX, XXX−XXX

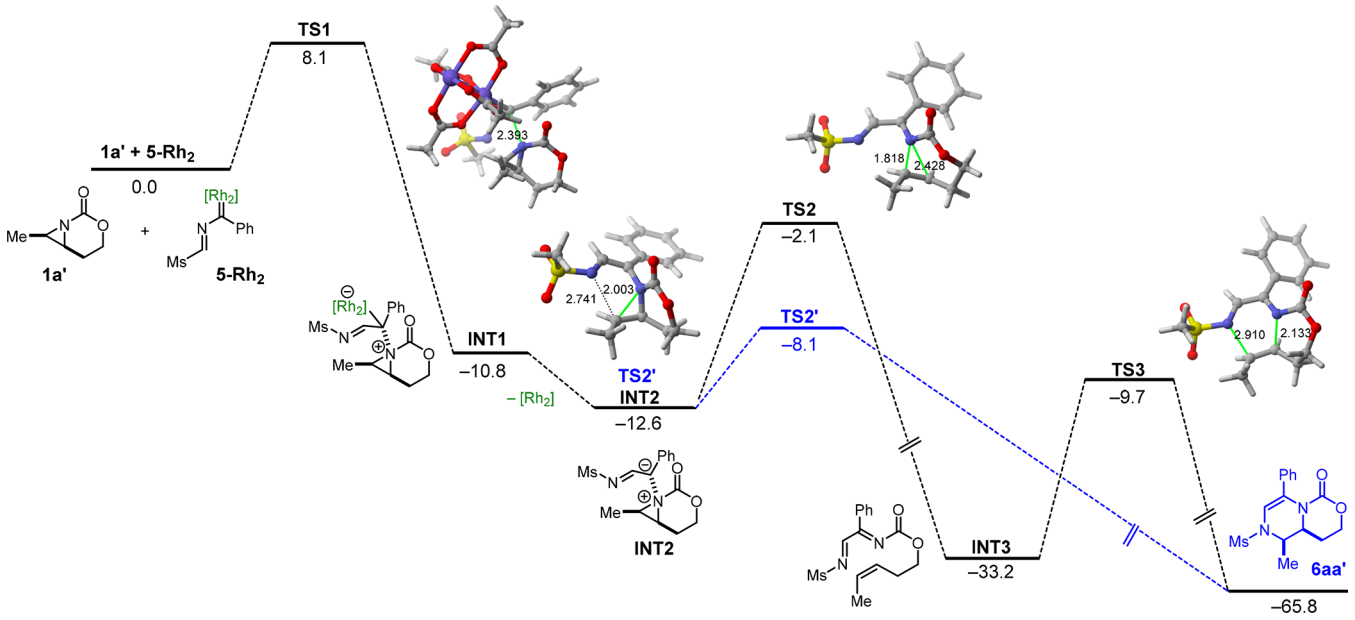
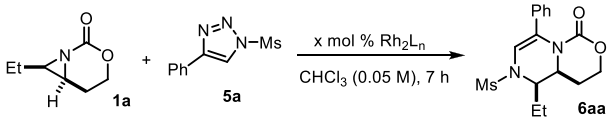


Figure 2. Computed reaction profile for the process involving **1a′** and dirhodium-bound carbene **5-Rh$_2$**. Relative free energies (ΔG, computed at 298.15 K and 1 M) and bond distances are given in kcal/mol and angstroms, respectively. All data have been computed at the SMD-B3LYP-D3/def2-SVP level.

Table 1. Reaction Optimization for Aziridine Expansion



entry	cat (mol %)	T (°C)	yield (%)	entry	cat (mol %)	T (°C)	yield (%)
1	$Rh_2(OAc)_4$ (6)	25	0[a]	6	$Rh_2(esp)_2$ (3)	70	78
2	$Rh_2(OAc)_4$ (6)	70	33[a]	7	$Rh_2(esp)_2$ (1)	70	79
3	$Rh_2(oct)_4$ (6)	70	51[a]	8	$Rh_2(esp)_2$ (0.5)	70	79
4	$Rh_2(TPA)_4$ (6)	70	44[a]	9	$Rh_2(esp)_2$ (0.1)	70	72
5	$Rh_2(esp)_2$ (6)	70	79[a] (75)				

[a]^{1}H NMR yield using mesitylene. All other yields are isolated yields.

of a bicyclic aziridine to the electrophilic carbene center to furnish the aziridinium ylide. Ring expansion then yields the dehydropiperazine.

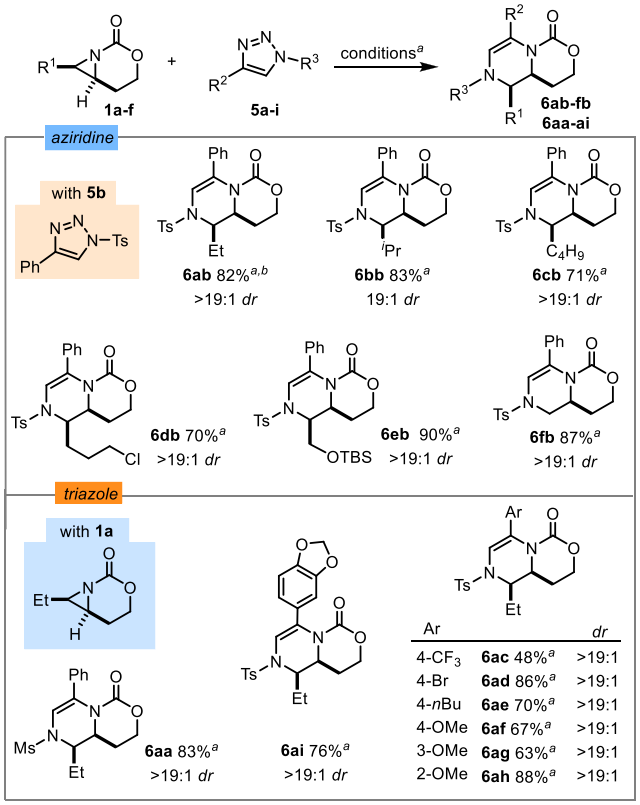
In initial attempts, treatment of *cis*-**1a** with **5a** and $Rh_2(OAc)_4$ at room temperature gave no conversion to the desired **6aa** (Table 1, entry 1). However, a 33% NMR yield of **6aa** was obtained when the reaction was heated to 70 °C (entry 2). Other commercially available rhodium catalysts known to promote carbene transfer were also tested (entries 3−5). Increased yields were observed in moving to the bulkier catalysts $Rh_2(oct)_4$, $Rh_2(tpa)_4$, and $Rh_2(esp)_2$. $Rh_2(esp)_2$ was selected as the optimal catalyst, and loadings gradually decreased to identify a good balance between yield and reaction time (entries 5−9). Although the loading of $Rh_2(esp)_2$ could be dropped to 0.1 mol % for **6aa**, other substrates required longer reaction times; thus, scope studies were carried out using 0.5 mol % of $Rh_2(esp)_2$.

With the optimized reaction conditions in hand, the aziridine scope was explored (Scheme 3, top). Silver-catalyzed nitrene transfer conditions developed in our group were used to prepare aziridines **1a−f** from the corresponding homoallylic carbamates.[24] Linear alkyl-substituted aziridines **1a** and **1c** gave dehydropiperazines **6ab** and **6cb** in good yield and excellent dr of >19:1. Increasing branching in the aziridine substituent of **1b** furnished **6bb** in good yield, suggesting this system tolerates steric pressure. Heteroatoms in the aziridine scaffold were well-tolerated, including an alkyl chloride in **1d** and a silyl-protected alcohol in **1e** to deliver **6db** and **6eb** in good yields as single diastereomers. Substitution on the aziridine precursor is not necessary, as **6fb** was produced in good yield and dr.

The scope of the *N*-sulfonyl-1,2,3-triazoles was examined with **1a** (Scheme 3, bottom). Mesyl- and tosyl-protected triazoles **5a** and **5b** furnished **6aa** and **6ab** in good yields. Due to easier removal of the *N*-tosyl group, a series of phenyl-substituted *N*-tosylated triazoles were explored to understand how the electronics and sterics of the triazole impact the reaction outcome. Triazoles **5h−j** and **5g**, substituted with electron-donating substituents, delivered **6ah−j** and **6ag** in good yield. The trifluoromethyl-substituted triazole **5c** gave **6ac** in a 48% yield, suggesting that electron-poor carbene precursors are not as effective for ring expansion, although an aryl bromide was tolerated to deliver **6ad**. Finally, carbene transfer with triazole **5i** was successful to furnish **6ai**. Demonstration of the scalability of the ring expansion was carried out on a 3.54 mmol scale using **1a** and **5b** to give a 75% yield of **6ab**.

https://dx.doi.org/10.1021/acs.orglett.0c01124
Org. Lett. XXXX, XXX, XXX−XXX

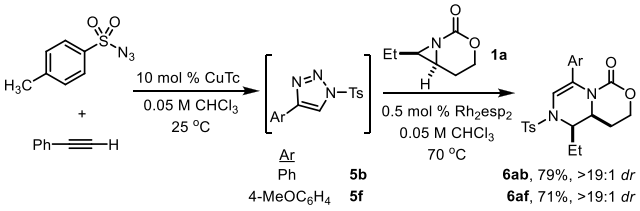
Scheme 3. Scope of the Aziridine Ring Expansion[a]



[a]Conditions: 0.5 mol% of Rh_2esp_2, 0.05 M $CHCl_3$, 70 °C. [b]Conducted on 0.5 g (3.5 mmol scale) of **1a**, 75%.

The dehydropiperazine synthesis was streamlined via a one-pot Cu-catalyzed azide−alkyne cycloaddition, followed by Rh-mediated carbene transfer/ring expansion (Scheme 4). Under

Scheme 4. One-Pot Synthesis from *p*-TsN_3



CuTC-catalyzed conditions, treatment of *p*-TsN_3 with phenylacetylene gave full conversion to **5b**. Addition of **1a** and $Rh_2(esp)_2$ to this mixture gave **6ab** in 79% yield and >19:1 dr. Similarly, *p*-methoxyphenylacetylene ultimately furnished **6ah** in 71% yield and excellent dr.

To gain a better understanding of the mechanism of the ring expansion, computational studies were carried out (Figure 2). The process involving *cis*-bicyclic aziridine **1a′** and dirhodium carbene **5-Rh$_2$**, formed from **5a** and $Rh_2(OAc)_4$, was explored. Similar to transformations involving related bicyclic aziridines (Scheme 1A),[20−22] the process begins with the exergonic (ΔG_R = −10.8 kcal/mol) nucleophilic addition of the aziridine nitrogen atom to the electrophilic carbene carbon atom of **5-Rh$_2$** via the transition state **TS1** ($\Delta G^{\ddagger}$ = 8.1 kcal/mol). This step forms ylide **INT1**, which evolves into the metal-free ylide **INT2** by the dissociation of the Rh_2 catalyst (ΔG_R = −1.8 kcal/mol). A similar barrierless Rh_2 dissociation was found by us in the processes involving related aziridines[21,22] and by others in the fates of related transition metal ylides.[25] Intermediate **INT2** may undergo a cheletropic extrusion similar to that observed initially by Watanabe (see Scheme 1A) to produce the alkene intermediate **INT3**. This highly exergonic reaction (ΔG_R = −20.6 kcal/mol) proceeds with a relatively low activation barrier ($\Delta G^{\ddagger}$ = 10.5 kcal/mol) via **TS2**, a saddle point associated with the rupture of both aziridine C−N bonds in a concerted manner. **INT3** is ideally suited to undergo [4 + 2] cycloaddition to produce the corresponding dehydropiperazine **6aa′**. This final aza-Diels−Alder reaction is also highly exergonic (ΔG_R = −32.6 kcal/mol) and occurs in a concerted fashion through **TS3** with a barrier of 23.5 kcal/mol, which is fully compatible with the temperatures (70 °C) used in this reaction. Despite this, an alternative reaction pathway was identified which directly produces the dehydropiperazine **6aa′** from ylide **INT2**. As shown in Figure 2, **INT2** undergoes a facile ($\Delta G^{\ddagger}$ = 4.5 kcal/mol) sigmatropic rearrangement via **TS2′** which involves the concomitant, yet highly asynchronous, breaking of the aziridine C−N bond and formation of the new C−N bond involving the NM moiety. Therefore, although both pathways are feasible within the experimental reaction conditions, our calculations suggest that the direct path involving **TS2′** is kinetically preferred over the stepwise mechanism involving **TS2** and **TS3**.

In conclusion, we have shown that the fate of aziridinium ylide intermediates depends on the structural features of the carbene precursor. Our initial attempt to prepare piperazine scaffold using a pyridotriazole carbene precursor gave an aziridinium ylide that preferentially underwent cheletropic extrusion to furnish a ketimine, as opposed to the desired ring expansion. Computations show this is due to the loss of aromaticity of the pyridine ring in the expansion pathway. By changing the nature of the carbene precursor to *N*-sulfonyl-1,2,3-triazoles, effective aziridine ring expansion provided access to densely substituted dehydropiperazines in excellent yields and diastereoselectivity. Computations suggest the mechanism involves a [1,4]-sigmatropic rearrangement of the key aziridinium ylide.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01124.

Experimental procedures, computational details, and characterization data for all new compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Jennifer M. Schomaker − *Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, United States;* orcid.org/0000-0003-1329-950X; Email: schomakerj@chem.wisc.edu

Israel Fernández − *Departamento de Orgánica I and Centro de en Química Avazanda (ORFEO−CINQA), Facultad de Ciencias, Universidad Complutense de Madrid, 28040 Madrid, Spain;* orcid.org/0000-0002-0186-9774; Email: israel@quim.ucm.es

https://dx.doi.org/10.1021/acs.orglett.0c01124
Org. Lett. XXXX, XXX, XXX−XXX

Authors

Hillary J. Dequina − *Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, United States*

Josephine Eshon − *Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, United States*

William T. Raskopf − *Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.0c01124

Author Contributions

§H.J.D. and J.E. contributed equally. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

J.M.S. thanks the NIH R01 GM11412 and the ACS-PRF No. 53146-ND1. The NMR facilities at UW-Madison are funded by the National Science Foundation (NSF; CHE-9208463, CHE-9629688) and the National Institutes of Health (NIH; RR08389-01). The Q-Exactive mass spectrometer was acquired with funds from an NIH-S10 award through the National Institutes of Health (NIH-1S10OD020022-1). I.F. acknowledges financial support from the Spanish MINECO-FEDER (Grants CTQ2016-78205-P and CTQ2016-81797-REDC).

■ REFERENCES

(1) Roiser, L.; Zielke, K.; Waser, M. Ammonium Ylide Mediated Cyclization Reactions. *Asian J. Org. Chem.* **2018**, *7*, 852−864.

(2) Li, A.-H.; Dai, L.-X.; Aggarwal, V. K. Asymmetric Ylide Reactions: Epoxidation, Cyclopropanation, Aziridination, Olefination, and Rearrangement. *Chem. Rev.* **1997**, *97*, 2341−2372.

(3) Michaelis, A.; Gimborn, H. V. Ueber Das Betain Und Cholin Dea Triphenylphosphins. *Ber. Dtsch. Chem. Ges.* **1894**, *27*, 272−277.

(4) Wittig, V. G.; Geissler, G. Zur Reaktionsweise Des Pentaphenyl-Phosphors Und Einiger Derivate. *Justus Liebigs Ann. Chem.* **1953**, *580*, 44−57.

(5) Wittig, G. Ursprung Und Entwicklung in Der Chemie Der Phosphin-Alkylene. *Angew. Chem.* **1956**, *68*, 505−508.

(6) Wittig, V. G.; Schollkopf, U. Über Triphenyl-phosphin-methylene als olefinbildende Reagenzien. *Chem. Ber.* **1954**, *87*, 1318−1330.

(7) Zhou, R.; He, Z. Advances in Annulation Reactions Initiated by Phosphorus Ylides Generated in Situ. *Eur. J. Org. Chem.* **2016**, *2016*, 1937−1954.

(8) Byrne, P. A.; Gilheany, D. G. The Modern Interpretation of the Wittig Reaction Mechanism. *Chem. Soc. Rev.* **2013**, *42*, 6670−6696.

(9) Burtoloso, A. C. B.; Dias, R. M. P.; Leonarczyk, I. A. Sulfoxonium and Sulfonium Ylides as Diazocarbonyl Equivalents in Metal- Catalyzed Insertion Reactions. *Eur. J. Org. Chem.* **2013**, *2013*, 5005−5016.

(10) (a) Sun, X.; Tang, Y. Ylide-Initiated Michael Addition−Cyclization Reactions beyond Cyclopropanes. *Acc. Chem. Res.* **2008**, *41*, 937−948. (b) Mcgarrigle, E. M.; Myers, E. L.; Illa, O.; Shaw, M. A.; Riches, S. L.; Aggarwal, V. K. *Chem. Rev.* **2007**, *107*, 5841−5883.

(11) *Nitrogen, Oxygen and Sulfur Ylide Chemistry. A Practical Approach in chemistry*; Clark, J. S., Ed.; Oxford University Press: Oxford, UK, 2002.

(12) (a) Lloyd, B.; Gosney, I.; Ormiston, R. A. Arsonium Ylides (with some mention also of arsinimines, stibonium and bismuthonium ylides). *Chem. Soc. Rev.* **1987**, *16*, 45−74. (b) He, H. S.; Chung, C. W. Y.; But, T. Y. S.; Toy, P. H. Arsonium Ylides in Organic Synthesis. *Tetrahedron* **2005**, *61*, 1385−1405.

(13) *The Chemistry of Organic Selenium and Tellurium Compounds.*; Rappoport, Z., Liebman, J. F., Marek, I., Patai, S., Eds.; Wiley: Hoboken, NJ, 2014; Vol. *4*, pp 1−657.

(14) (a) Qiu, G.; Kuang, Y.; Wu, J. *N*-Imide Ylide-Based Reactions: C-H Functionalization, Nucleophilic Addition and Cycloaddition. *Adv. Synth. Catal.* **2014**, *356*, 3483−3504. (b) Adrio, J.; Carretero, J. C. Recent advances in the catalytic asymmetric 1,3-dipolar cycloaddition of azomethine ylides. *Chem. Commun.* **2014**, *50*, 12434−12446.

(15) Jacobs, J.; Van Hende, E.; Claessens, S.; De Kimpe, N. Pyridinium Ylids in Heterocyclic Synthesis. *Curr. Org. Chem.* **2011**, *15*, 1340−1362.

(16) Moderhack, D. *N*-Ylides of 1,2,3-Triazole and Tetrazoles− an overview. *Heterocycles* **2014**, *89*, 2053−5089.

(17) Hata, Y.; Watanabe, M. Fragmentation Reaction of Aziridinium Ylids. *Tetrahedron Lett.* **1972**, *13*, 3827−3830.

(18) (a) Woodward, R. B.; Hoffmann, R. The Conservation of Orbital Symmetry. *Angew. Chem., Int. Ed. Engl.* **1967**, *8*, 781−853. (b) Sweeney, J. B. Sigmatropic Rearrangements of "onium" Ylids. *Chem. Soc. Rev.* **2009**, *38*, 1027−1038.

(19) Rowlands, G. J; Kentish Barnes, W. Studies on the [2,3]-Stevens Rearrangement of Aziridinium Ions. *Tetrahedron Lett.* **2004**, *45*, 5347−5350.

(20) Schmid, S. C.; Guzei, I. A.; Schomaker, J. M. A Stereoselective [3 + 1] Ring Expansion for the Synthesis of Highly Substituted Methylene Azetidines. *Angew. Chem.* **2017**, *129*, 12397−12401.

(21) Schmid, S. C.; Guzei, I. A.; Fernández, I.; Schomaker, J. M. Ring Expansion of Bicyclic Methyleneaziridines via Concerted, Near-Barrierless [2,3]-Stevens Rearrangements of Aziridinium Ylides. *ACS Catal.* **2018**, *8*, 7907−7914.

(22) Eshon, J.; Nicastri, K. A.; Schmid, S. C.; Raskopf, W. T.; Guzei, I. A.; Fernández, I.; Schomaker, J. M. Intermolecular [3 + 3] Ring-Expansion of Aziridines to Dehydropiperidines through the Intermediacy of Aziridinium Ylides. *Nat. Commun.* **2020**, *11*, 1−8.

(23) (a) Davies, H. M. L.; Alford, J. S. Reactions of metallocarbenes derived from *N*-sulfonyl-1,2,3-triazoles. *Chem. Soc. Rev.* **2014**, *43*, 5151−5162. (b) Parr, B. T.; Green, S. A.; Davies, H. M. L. Rhodium-Catalyzed Conversion of Furans to Highly Functionalized Pyrroles. *J. Am. Chem. Soc.* **2013**, *135*, 4716−4718. (c) Spangler, J. E.; Davies, H. M. L. Catalytic Asymmetric Synthesis of Pyrroloindolines via a Rhodium (II)-Catalyzed Annulation of Indoles. *J. Am. Chem. Soc.* **2013**, *135*, 6802−6805. (d) Zibinsky, M.; Fokin, V. Sulfonyl-1,2,3-Triazoles: Convenient Synthones for Heterocyclic Compounds. *Angew. Chem., Int. Ed.* **2013**, *52*, 1507−1510. (e) Chuprakov, S.; Kwok, S. W.; Fokin, V. V. Transannulation of 1-Sulfonyl-1,2,3-triazoles with Heterocumulenes. *J. Am. Chem. Soc.* **2013**, *135*, 4652−4655. (f) Miura, T.; Hiraga, K.; Biyajima, T.; Nakamuro, T.; Murakami, M. Regiocontrolled Synthesis of Polysubstituted Pyrroles Starting from Terminal Alkynes, Sulfonyl Azides, and Allenes. *Org. Lett.* **2013**, *15*, 3298−3301. (g) Alford, J. S.; Spangler, J. E.; Davies, H. M. L. Conversion of Cyclic Ketones to 2,3-Fused Pyrroles and Substituted Indoles. *J. Am. Chem. Soc.* **2013**, *135*, 11712−11715.

(24) Ju, M.; Weatherly, C. D.; Guzei, I. A.; Schomaker, J. M. Chemo- and Enantioselective Intramolecular Silver-Catalyzed Aziridinations. *Angew. Chem., Int. Ed.* **2017**, *56*, 9944−9948.

(25) (a) Liang, Y.; Zhou, H.; Yu, Z. Why Is Copper(I) Complex More Competent Than Dirhodium(II) Complex in Catalytic Asymmetric O−H Insertion Reactions? A Computational Study of the Metal Carbenoid O−H Insertion into Water. *J. Am. Chem. Soc.* **2009**, *131*, 17783−17785. (b) Alcaide, B.; Almendros, P.; Fernández, I.; Campo, T. M.; Palop, G.; Toledano-Pinedo, M.; Delgado-Martínez, P. Chemoselectivity Switching in the Rhodium-Catalyzed Reactions of 4-Substituted-1-sulfonyl-1,2,3-triazoles with Allenols: Noticeable Differences between 4-Acyl- and 4-Aryl-Triazoles. *Adv. Synth. Catal.* **2019**, *361*, 1160.