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Anionic 5-*endo-dig* cyclizations: an experimental investigation of in-plane aromaticity involving a non-enolate carbanion nucleophile†

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Cyclitive additions of aliphatic carbanions to non-electrophilic carbon–carbon triple bonds under mild, transition-metal-free conditions are described for the first time. These results confirm theoretical models that invoke in-plane aromaticity to predict the favorability of 5-*endo-dig* reactions in these systems. In contrast to related Conia-ene cyclizations (5-enolexo-*endo-dig*), our results generally led to cyclic and allene products in near parity ratios across a broad range of substrates, suggesting that cyclization may proceed *via* an early ambimodal transition state. Experimental results are presented with a view to refining existing mechanistic models for this growing class of alkyne reactions.

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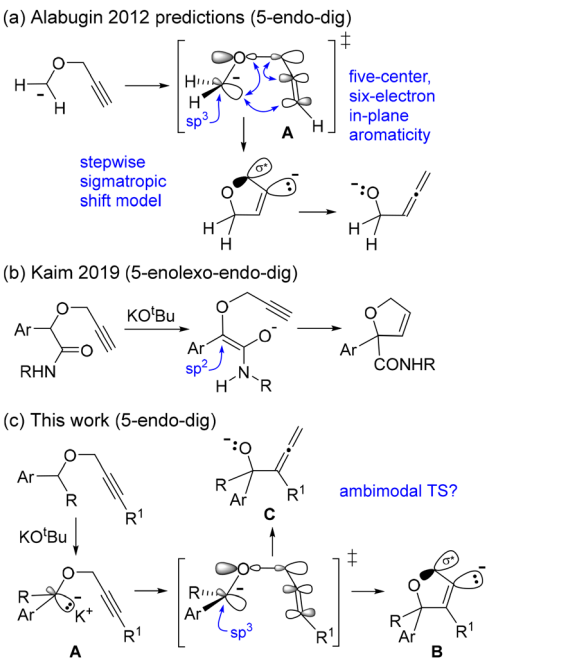
Introduction

Since Baldwin's landmark paper in 1976,[1] 5-*endo-dig* cyclizations involving sp^3 carbon nucleophiles have not been reported despite extensive computational studies by Alabugin and coworkers predicting their favorability.[2] These modeling studies of 5-*endo-dig* reactions invoke a transition-state involving in-plane aromaticity.[3] Specifically the six electrons in this "Sigma" aromaticity are the result of a localized lone pair, acting as a nucleophile, a Sigma carbon–oxygen bond, and an alkynyl π-bond (Scheme 1a). In these systems, Baldwin recognized the differences in reactivity between localized and delocalized attacking nucleophiles, citing variations in intramolecular orbital alignment between sp^3 and sp^2 nucleophiles. From these considerations, Baldwin distinguishes enolate nucleophiles using enolexo and enolendo terminology.[4] In general, cyclizations proceeding through enolate intermediates are classified as Conia-ene reactions. In the case of alkyne substrates, these reactions largely lead to *exo* products when mediated by transition metals.[5] Such reactions would be designated as enolexo-*exo-dig* cyclizations. A small number of metal catalyzed Conia-ene reactions also give 5-enolexo-*endo-dig* cyclizations.[6] Kaim reports the only example of a base mediated 5-enolexo-*endo-dig* cyclization (Scheme 1b).[7] However, no examples of alkyne cyclization have appeared in the literature where the nucleophilic carbon is not part of an enolate system (as in the Conia-ene).

We sought to assess the reactivity of a 5-*endo-dig* reaction involving an sp^3 carbanion nucleophile such as **A** (Scheme 1c). Synthetic approaches to produce non-resonance stabilized carbanions[8] have been developed, such as decarboxylative methods under collision induced dissociation (CID)[9] and desi-



Scheme 1 Carbanion nucleophile geometry in *endo-dig* reaction mechanisms.

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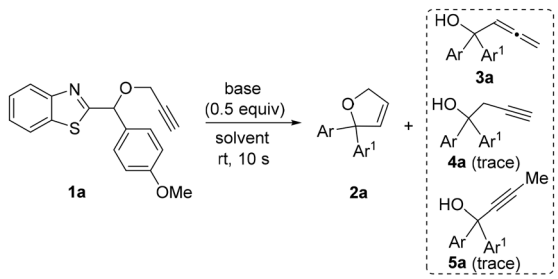
lylation (Depuy reaction) under fluorination conditions.[10] Direct deprotonation of aryl substituted sp^3 hybridized carbon acids is also a well-known strategy to generate carbanions,[11] and effectively used in synthesis.[12] Carbanions produced *via* the latter method have been computationally established to be sp^3 hybridized in the presence of metal cations.[13] Using this deprotonative carbanion forming strategy, we report 5-*endo-dig* cyclizations leading to 2,5-dihydrofurans and sigmatropic products, addressing, for the first time, theoretical predictions for this reaction class.

Results and discussion

To identify optimal reaction conditions, propargyl ether **1a** was prepared[14] and exposed to a variety of bases and solvents. We were gratified to observe that one of the first bases examined, potassium *tert*-butoxide (KO^{t}Bu), led to cyclized product **2b** and to [2,3]-sigmatropic shift product **3a** as well as trace amounts of its isomers **4a** and **5a** (Table 1, entry 1). It was quickly realized that acetonitrile (MeCN) was the optimal solvent for this transformation, leading to a near equimolar ratio of cyclic to [2,3]-sigmatropic shift products (entry 7).

Table 1 Optimization of reaction conditions



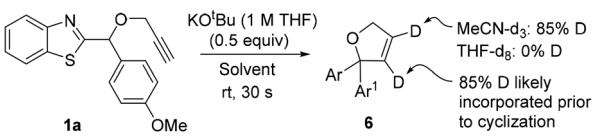
Entry	Solvent	Base	% yield of **2a** [a]	% yield of **3a–5a** [b]
1	Toluene[e]	KO^{t}Bu	6	7
2	Toluene	KO^{t}Bu[c,d]	9	70
3	THF[f]	KO^{t}Bu	6	24
4	THF	KO^{t}Bu[c,d]	35	59
5	Acetone[g]	KO^{t}Bu	8	28
6	Acetone	KO^{t}Bu[c,d]	34	47
7	MeCN	KO^{t}Bu	46	41
8	DCM	KO^{t}Bu	14	20
9	MeCN	NaO^{t}Bu	45	46
10	MeCN	LiO^{t}Bu	0	0
11	MeCN	KO^{i}Pr	0	0
12	MeCN	KOH	0	0
13	MeCN	NaH	0	0
14	MeCN	K_2CO_3	0	0
15	MeCN	DBU	0	0
16	MeCN	KO^{t}Bu[c]	48	44
17	THF	KO^{t}Bu[c]	34	48
18	THF	NaO^{t}Bu[c]	37	36

[a] Isolated yields. [b] Yields based on an isolated mixture of isomers **3a** and trace amounts of **4a** and **5a**. [c] Additive 18-C-6 present in a 1.5 : 1 ratio with the base. [d] 2.0 eq. of base. [e] 79% **1a** remaining. [f] 38% **1a** remaining. [g] 54% **1a** remaining.

We found that the reaction was completed in under 10 seconds at room temperature when treated with a solution of KO^{t}Bu (1 M in THF) and that longer reaction times led to extensive decomposition of the sigmatropic products. With the exception of NaO^{t}Bu, all other bases examined failed to give any products in MeCN at room temperature or upon warming. Our studies involving deuterated MeCN reveal that KO^{t}Bu does slowly deprotonate that solvent. To evaluate whether the conjugate base of MeCN is the active species mediating the present cyclization reaction, we treated MeCN with KO^{t}Bu and, after varying amounts of time, added that mixture to a solution of starting material **1a** in MeCN. While trace amounts of products **2a** and **3a** were formed after 30 min, the reactions mostly produced decomposition products. The key to success in this reaction was to add KO^{t}Bu (as a THF solution) to the substrate dissolved in MeCN, allowing as little time as possible for KO^{t}Bu to mix with the MeCN reaction solvent. This preference in order of addition may also be related to the aggregation state[15] of KO^{t}Bu affecting its reactivity. Indeed, it is known that monomeric forms of KO^{t}Bu increases its basicity.[16] Thus, KO^{t}Bu treated with additive 18-crown-6 (18-C-6) in THF produced **2a** (34%) and **3a–5a** (48%), an increase compared to no additive (compare entries 3 and 17). However, the addition of 18-C-6 to **1a** in MeCN made no appreciable difference (compare entries 7 and 16). A similar but less pronounced result was observed with NaO^{t}Bu (compare entries 9 and 18). Interestingly, in toluene (entries 1 and 2), the crown ether drove the reaction to completion and strongly favored 2,3-shift products.

Except for our toluene experiments, these results suggest that product ratios are generated prior to any protonation step since these ratios remain largely unchanged in either proton abundant (MeCN) and proton-free (THF with 18-C-6) media. When KO^{t}Bu was pre-treated with 18-C-6 and added to substrate **1a** dissolved in MeCN (entry 16) the reaction produces **2a** (48%) and **3a** (44%). The MeCN solvent is sufficiently acidic such that its deuterated form leads to extensive deuterium incorporation into product in the presence of KO^{t}Bu (Scheme 2). It seems reasonable to expect that products **2a** and **3a** would be formed, at least in part, by utilizing the solvent as a proton source to a greater degree than ^{t}BuOH. By contrast, the reaction conducted in THF with 18-crown-6 (entry 17) has no solvent proton source and still leads to nearly the same outcome, namely **2a** (34%) and **3a** (48%).

As mentioned, studies in deuterated MeCN demonstrate that this solvent acts as a proton donor in the present reaction (Scheme 2). Studies revealed 85% deuterium incorporation to give cyclic product **6**; the conjugate acid of the base (*i.e.*, HO^{t}Bu) is probably the source of the remaining 15% proton



Scheme 2 Deuterium incorporation study.

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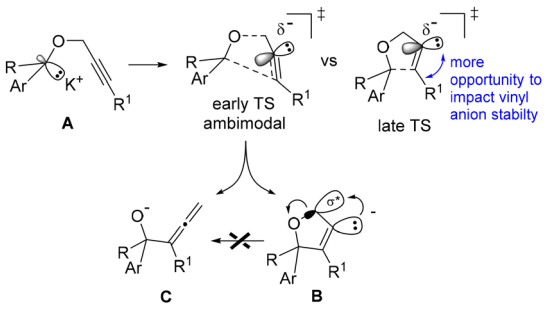
incorporation. We note that studies of **1a** in deuterated MeCN in the presence of LiO^{t}Bu, while not leading to any product formation (Table 1, entry 10), gave deuterium incorporation at the terminal alkyne carbon. Importantly, when **3a** was isolated and exposed to reaction conditions, it gave no cyclic product **2a** but rather partially isomerized to **4a** and **5a**. We were unable to find any conditions with KO^{t}Bu (heat, prolonged reaction times, multiple base equivalents) or with more powerful bases such as *n*-BuLi leading to the conversion of **2a** to its acyclic isomers.

To date, we have not identified any synthetically useful conditions that led to a complete conversion of **1a** to products in a ratio of **2a**:**3a–5a** that was other than near parity. This includes prolonged reaction times,[17] higher/lower temperatures, changing base stoichiometries, and a wide range of solvents and cosolvents.

We next sought to elucidate the role of substrate structure on the ratio of cyclic to [2,3]-sigmatropic shift products. Scaffolds were selected containing a variety of aryl and alkyl substituents such that the benzylic position remained acidic enough for KO^{t}Bu to bring about product formation. Using our optimized conditions, nearly every combination of substituents led to the same ratio of cyclic (**2**) to shift products (**3–5**). For example, substrate **1c** was designed to assess the impact at the benzylic position in terms of steric hindrance and diminished carbanion stabilization upon deprotonation. However, the reaction of **1c** went to completion giving very similar results as bisaryl substrate **1a**, in both cases a ratio of 1.1 for products **2** to **3–5** was observed. A variety of aromatic heterocycles in addition to benzothiazole leads to product formation such as benzothiophene (**1d**), thiazole (**1e**) and thiophene (**1f**). In all cases, the change in the electronic characteristics of the heterocycle did not lead to any appreciable differences in product ratios. The introduction of a *para* CF_3, a strongly inductive electron withdrawing group, in substrate **1g** led to virtually no difference relative to **1h**, containing a *para* OMe, a powerful electron donating group. In both cases, the overall yields and product ratios were comparable. A comparison of substrate **1c** with **1i** reveals that extensive steric crowding may have an impact on product ratio. In the case of **1i**, cyclization leading to a crowded **2i**, appears to be less favorable to the formation of sigmatropic allene **3i**. In general, however, the electronic and steric environment of the benzylic nucleophile carbon does not appear to play a significant role in product distribution.

Our substrate studies with internal alkynes (**1g–1j**) also allowed for the evaluation of the role played by hyperconjugation in stabilizing the hypothesized transition states (TS) in the present reaction. Specifically, we argue that stabilization of vinyl anion **B** by donation of electron density from the lone pair in the σ^* C–R^1 bond favors 5-*endo-trig* cyclization products (Scheme 3). Applying this argument to possible transitions states leading to products **2–5**, one would expect that in a late TS the R^1 substituent would play a greater role in cyclic product stabilization relative to an early TS. In the context of a stepwise transition state, Alabugin reported the energy from



Scheme 3 Early *versus* late TS and possible ambimodal TS.

the vinyl anion can be alleviated with Sigma acceptor substituents, thus leading to favoring cyclic product. Meanwhile, with Sigma donor substituents, the highly energetic vinyl anion will lead to C–O bond rupture and favor allene formation.[3] An evaluation of products from **1d** (R^1 = H), **1g** (R^1 = Me), and **1j** (R^1 = Ph) suggest there is little impact of the R^1 group on product ratio. Interestingly, cyclization reactions in all-carbon systems in which the carbanion is generated *via* lithium halogen exchange led only to 4-*exo-dig* products with substrates bearing alkynyl substituents (*e.g.*, Ph or TMS) capable of stabilizing an *exo* vinyl anion.[18] This suggests that Ph may play a relatively important role as a vinyl stabilizing group. However, starting material **1j**, which also contains a phenyl group on the alkyne, led to exclusive *endo* cyclization and [2,3]-sigmatropic shift products (Table 2), suggesting that the Ph group was not as important for stabilization as the endocyclic C–O bond or aromatic stabilization. Similarly, the ratio of products formed from **1a** (R^1 = H) and **1h** (R^1 = Me) were largely unaffected by the R^1 substituent. These data support an early TS geometry, possibly ambimodal,[19] that minimizes overlap of the growing charge density with the σ^* C–R^1 bond.

Theoretical and modeling studies by Alabugin suggest a stepwise mechanism in which anionic 5-*endo-dig* ring closures can, in some cases, proceed to give [2,3]-sigmatropic shift products.[3] This would take place by endocyclic donation of the vinyl anion lone pair of **B** to the adjacent σ^* C–O bond to promote a ring-opening scission of that bond, leading to allene product **C** (Scheme 3). If the **B** to **C** conversion is stepwise, then the rate of that conversion should depend on the stability of anion **B**. However, as discussed above, our data indicate that the ratio of **B**:**C** (protonated forms) is virtually independent of the nature of the R^1 substituent, which is inconsistent with the stepwise mechanism. As mentioned above, attempts to produce anionic intermediates such as **B** from **2a** were unsuccessful, resulting in nearly 100% recovery of the cyclic starting material. Additionally, our efforts to convert **3a** to an intermediate such as **C** to then produce **2a** were fruitless and only resulted in partially isomerization to **4a** and **5a**. We suggest that products **B** and **C** are perhaps produced simultaneously *via* a concerted ambimodal TS. Similar explanations have been put forth by Houk to explain the Diels–Alder reaction of butadiene and allene.[19] In this conception,

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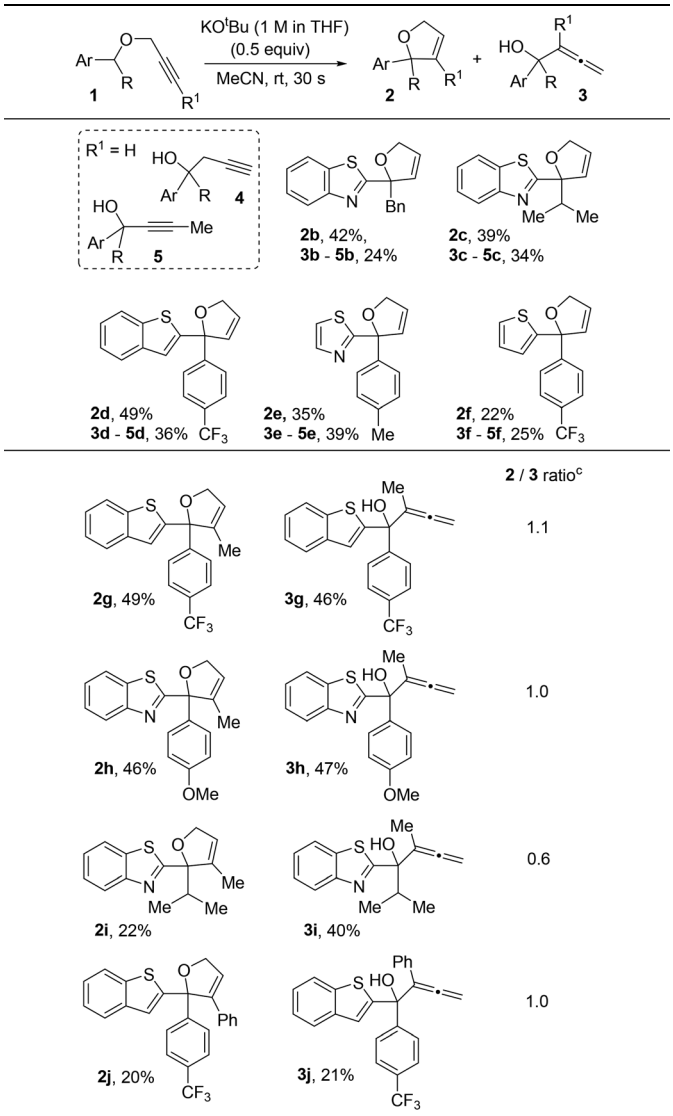
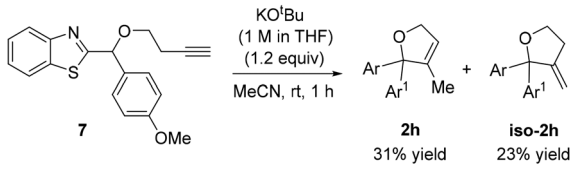
Table 2 Reaction scope of substrates *via* a 5-*endo-dig* mechanism leading to 2,5-unsaturated cyclic ethers[a,b,c]



[a] All reactions performed at 0.1 M concentration of propargyl ethers **1**. [b] All yields reported are isolated yields. [c] Isomers **4** and **5** not observed for internal propargyl ethers.

the ratio of **B** : **C** would be based on factors influencing the TS and not depend on the conversion of **B** to **C**.

In an effort to further evaluate the in-plane aromaticity model of Alabugin, we examined the reactivity of homopropargyl ether **7** (Scheme 4). The additional methylene was expected to remove the ability of the substrate to achieve a 6-electron cyclic array in the TS. To our surprise, the addition of KO^{t}Bu under mild conditions cyclized this substrate in a 5-*exo-dig* manner leading to furan **2h** and its isomer **iso-2h** along with a trace of the 1,3-diene isomer of **7**. Experiments reveal that isomers **2h** and **iso-2h** are in equilibrium under the reaction conditions.



Scheme 4 Homopropargyl ether **7** leads to 5-*exo-dig* products.

Conclusions

Predictions made more than a decade ago have finally been answered in this work where we demonstrate a base-mediated 5-*endo-dig* cyclization (non-Conia-ene) involving a carbon nucleophile, most likely in the pyramidal state. In terms of product yields and distribution, the present reaction appears to be relatively insensitive to wide-ranging variations in substrate electronics/sterics and to proton availability. This suggests that product distribution may be established prior to any protonation step, possibly through a concerted mechanism. The facility with which this 5-*endo-dig* reaction proceeds appears to confirm theoretical modeling studies featuring in-plane aromaticity. While the homopropargyl result (Scheme 4) does not allow for this aromatic stabilizing effect, the *exo-dig* reaction proceeds with surprising facility. Finally, additional theoretical efforts are also needed to differentiate between 5-*endo-dig* reaction pathways advancing in a stepwise fashion or through a possible early ambimodal transition state.

Author contributions

S. D. L. and P. M. conceived the project. K. M. N. and S. Q. H. performed the experimental studies. S. D. L. supervised the research. K. M. N. wrote the original draft which was edited by S. D. L.

Conflicts of interest

There are no conflicts to declare.

Data availability

^{1}H and ^{13}C NMR, HRMS spectral data for all new compounds, and experimental details are available in the ESI.†

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References

1 J. E. Baldwin, Rules for ring closure, *J. Chem. Soc., Chem. Commun.*, 1976, (18), 734, DOI: 10.1039/c39760000734.

2 K. Gilmore and I. V. Alabugin, Cyclizations of Alkynes: Revisiting Baldwin's Rules for Ring Closure, *Chem. Rev.*, 2011, **111**(11), 6513–6556, DOI: 10.1021/cr200164y.

3 K. Gilmore, M. Manoharan, J. I. C. Wu, P. V. R. Schleyer and I. V. Alabugin, Aromatic Transition States in Nonpericyclic Reactions: Anionic 5-Endo Cyclizations Are Aborted Sigmatropic Shifts, *J. Am. Chem. Soc.*, 2012, **134**(25), 10584–10594, DOI: 10.1021/ja303341b.

4 J. E. Baldwin and L. I. Kruse, Rules for ring closure. Stereoelectronic control in the endocyclic alkylation of ketone enolates, *J. Chem. Soc., Chem. Commun.*, 1977, (7), 233, DOI: 10.1039/c39770000233.

5 D. Hack, M. Bluemel, P. Chauhan, A. R. Philipps and D. Enders, Catalytic Conia-ene and related reactions, *Chem. Soc. Rev.*, 2015, **44**(17), 6059–6093, DOI: 10.1039/C5CS00097A.

6 For some recent examples see: (*a*) S. Tamke, Z.-W. Qu, N. A. Sitte, U. Floerke, S. Grimme and J. Paradies, Frustrated Lewis Pair-Catalyzed Cycloisomerization of 1,5-Enynes via a 5-endo-dig Cyclization/Protodeborylation Sequence, *Angew. Chem., Int. Ed.*, 2016, **55**(13), 4336–4339, DOI: 10.1002/anie.201511921; (*b*) B. Ma, Z. Wu, B. Huang, L. Liu and J. Zhang, Gold-catalysed facile access to indene scaffolds via sequential C-H functionalization and 5-endo-dig carbocyclization, *Chem. Commun.*, 2016, **52**(60), 9351–9354, DOI: 10.1039/c6cc04034a; (*c*) M. Cao, A. Yesilcimen and M. Wasa, Enantioselective Conia-Ene-Type Cyclizations of Alkynyl Ketones through Cooperative Action of B(C6F5)3, N-Alkylamine and a Zn-Based Catalyst, *J. Am. Chem. Soc.*, 2019, **141**(10), 4199–4203, DOI: 10.1021/jacs.8b13757; (*d*) A. S. Narode, Y.-S. Ho, M.-J. Cheng and R.-S. Liu, Gold-Catalyzed Addition of β-Oxo Enols at Tethered Alkynes via a Non-Conia-ene Pathway: Observation of a Formal 1,3-Hydroxymethylidene Migration, *Org. Lett.*, 2023, **25**(9), 1589–1594, DOI: 10.1021/acs.orglett.3c00504.

7 L. B. Gaied, N. Fincias, J. Garrec and L. E. Kaim, 5-endo-dig Cyclization of O-Propargyl Mandelic Acid Amides towards 2,5-Dihydrofurans, *Eur. J. Org. Chem.*, 2019, (47), 7656–7665, DOI: 10.1002/ejoc.201901397.

8 Z. Tian and S. R. Kass, Carbanions in the Gas Phase, *Chem. Rev.*, 2013, **113**(9), 6986–7010, DOI: 10.1021/cr4000896.

9 (*a*) R. R. Squires, Gas-phase carbanion chemistry, *Acc. Chem. Res.*, 1992, **25**(10), 461, DOI: 10.1021/ar00022a005; (*b*) S. T. Graul and R. R. Squires, Generation of alkyl carbanions in the gas phase, *J. Am. Chem. Soc.*, 1990, **112**(7), 2506, DOI: 10.1021/ja00163a006.

10 (*a*) M. M. Meyer and S. R. Kass, Enolates in 3-D: An Experimental and Computational Study of Deprotonated 2-Adamantanone, *J. Org. Chem.*, 2010, **75**(12), 4274–4279, DOI: 10.1021/jo100953y; (*b*) C. H. DePuy, V. M. Bierbaum, L. A. Flippin, J. J. Grabowski, G. K. King, R. J. Schmitt and S. A. Sullivan, Gas-phase reactions of anions with substituted silanes, *J. Am. Chem. Soc.*, 1980, **102**(15), 5012, DOI: 10.1021/ja00535a031; (*c*) C. H. DePuy, V. M. Bierbaum, L. A. Flippin, J. J. Grabowski, G. K. King and R. J. Schmitt, Generation of specific isomeric carbanions in the gas phase, *J. Am. Chem. Soc.*, 1979, **101**(21), 6443, DOI: 10.1021/ja00515a054.

11 F. G. Bordwell, J. Cheng, G. Z. Ji, A. V. Satish and X. Zhang, Bond dissociation energies in DMSO related to the gas phase values, *J. Am. Chem. Soc.*, 1991, **113**(26), 9790–9795, DOI: 10.1021/ja00026a012.

12 M. N. Alam, K. M. Lakshmi and P. Maity, A removable functional group strategy for regiodivergent Wittig rearrangement products, *Org. Biomol. Chem.*, 2018, **16**(46), 8922–8926, DOI: 10.1039/c8ob02221f.

13 K. B. Lipkowitz, C. Uhegbu, A. M. Naylor and R. Vance, Structural features of benzylic carbanions. A theoretical study, *J. Comput. Chem.*, 1985, **6**(6), 662, DOI: 10.1002/jcc.540060621.

14 This substrate and related analogs were synthesized in 60–80% overall yields in two steps; see ESI† for experimental details.

15 (*a*) P. Schmidt, L. Lochmann and B. Schneider, Structure and vibrational spectra of the sodium and potassium tert-butoxides, *J. Mol. Struct.*, 1971, **9**(4), 403, DOI: 10.1016/0022-2860(71)87030-8; (*b*) J. Klett, Structural Motifs of Alkali Metal Superbases in Non-coordinating Solvents, *Chem. – Eur. J.*, 2021, **27**(3), 888–904, DOI: 10.1002/chem.202002812.

16 J. Ahmed, A. K. Swain, A. Das, R. Govindarajan, M. Bhunia and S. K. Mandal, A K-arylacetylide complex for catalytic terminal alkyne functionalization using KO^{t}Bu as a pre-catalyst, *Chem. Commun.*, 2019, **55**(92), 13860–13863, DOI: 10.1039/c9cc07833a.

17 As mentioned, prolonged reaction times led to a decomposition of the sigmatropic shift products thus artificially increasing the ratio of cyclic product but ultimately lowering overall conversions.

18 (*a*) W. F. Bailey and T. V. Ovaska, Intramolacular Addition of Alkyllithiums to Acetylenes: Regiospecific 4-, 5-, and 6-Exo-Dig Cyclizations, *Tetrahedron Lett.*, 1990, **31**, 627; (*b*) W. F. Bailey and T. V. Ovaska, Cyclization of Acetylenic Alkyllithiums, *J. Am. Chem. Soc.*, 1993, **115**, 3080.

19 H. V. Pham and K. N. Houk, Diels–Alder Reactions of Allene with Benzene and Butadiene: Concerted, Stepwise, and Ambimodal Transition States, *J. Org. Chem.*, 2014, **79**(19), 8968–8976, DOI: 10.1021/jo502041f.