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Highly Strained *para*-Phenylene-Bridged Macrocycles from Unstrained 1,4-Diketo Macrocycles

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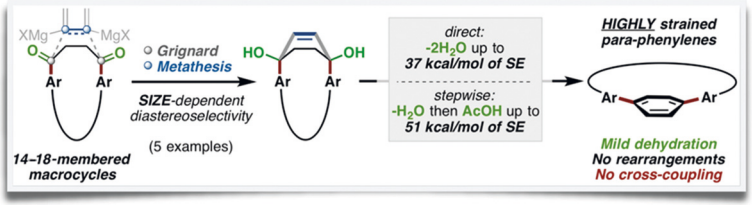

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Abstract The conversion of macrocyclic 1,4-diketones to highly strained *para*-phenylene rings has recently been reported by our laboratory. This synthetic strategy represents a non-cross-coupling-based approach to arene-bridged macrocycles, and an alternative to palladium- and nickel-mediated processes. In this Synpacts article we discuss the development of endgame aromatization protocols for the synthesis of increasingly strained arene systems, as well as potential advantages of the macrocyclic 1,4-diketone approach to selectively functionalized benzenoid macrocycles for future complexity building reactions.

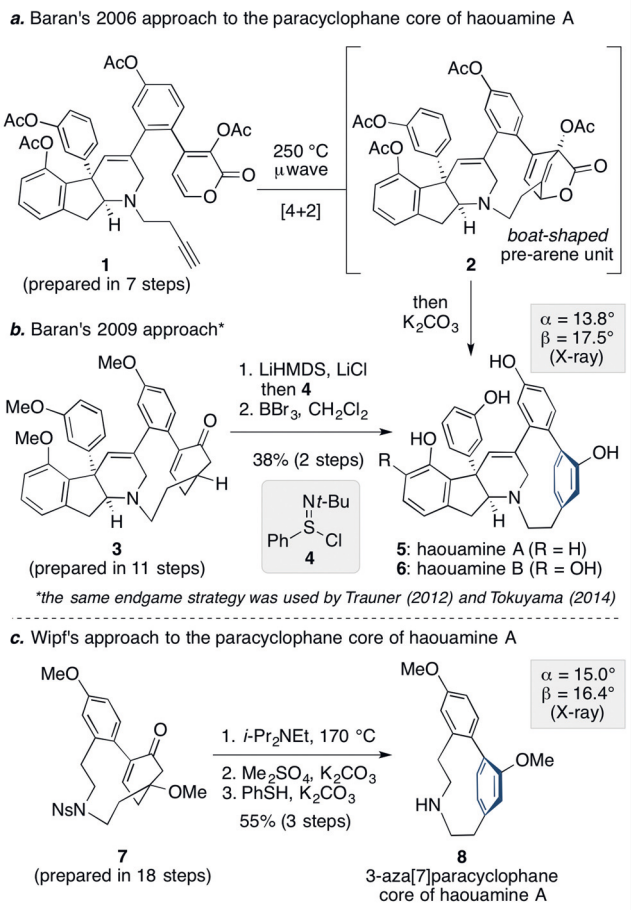
Key words macrocycles, 1,4-diketones, dehydrative aromatization, *para*-phenylenes, rearrangement reactions, strain energy

Bradley L. Merner (center) received his undergraduate and graduate training at Memorial University. After completing his Ph.D. under the direction of Prof. Graham J. Bodwell in 2010, he moved to the Université de Montréal for postdoctoral studies in the laboratory of Prof. Stephen Hanessian. In 2013, he began his independent career as an assistant professor at Auburn University and in 2016 he was awarded the James E. Land Professorship of chemistry and biochemistry. His research program is focused on target-oriented chemical synthesis, spanning the fields of medicinal chemistry and nanoscale science.
Nirmal Kumar Mitra (right) graduated from the University of Dhaka with B.S and M.S. degrees in 2005 and 2007, respectively. In 2013, Nirmal was amongst the first cohort of graduate students to join Prof. Merner's research group. Since then he has been utilizing macrocyclic 1,4-diketones in the synthesis of strained arene-bridged systems, and is currently pursuing their use in developing novel π-extension methodology.
Caroline P. Merryman (left) received her undergraduate training at the College of William and Mary, where she conducted undergraduate research in the laboratory of Prof. Robert Hinkle. In 2014, she enrolled in the Ph.D. program at Auburn University and is currently in her third year of study. Caroline's research is focused on the synthesis of highly strained benzenoid macrocycles and she is currently pursuing the synthesis of [4]cycloparaphenylene in Prof. Merner's laboratory.

1 Introduction

The synthesis of strained macrocyclic benzenoid systems, particularly those containing arene-arene-linked or biaryl units, using direct cross-coupling reactions has proven to be a challenge for chemical synthesis.[1] The limitations of cross-coupling-based approaches to strained arene-bridged systems (biaryl or polyaryl) are exemplified by the haouamine alkaloids and the [*n*]cycloparaphenylenes ([*n*]CPPs) (Schemes 1 and 2). The need to bend the arene unit upon C_{sp^2}–C_{sp^2} bond formation via rigid precursor substrates, in the case of the haouamines, has led to many incomplete or failed (total) synthetic approaches.[2] The assembly of the strained 3-aza[7]paracyclophane (phenol) core of the natural product was cleverly achieved by Baran and coworkers, through the intermediacy of a (boat-shaped) bridged bicyclo[2.2.2]-1-oxaoctan-2-one **2**, which was prepared by an intramolecular Diels–Alder reaction of **1** (Scheme 1, a).[3] After cheletropic elimination of carbon diox-

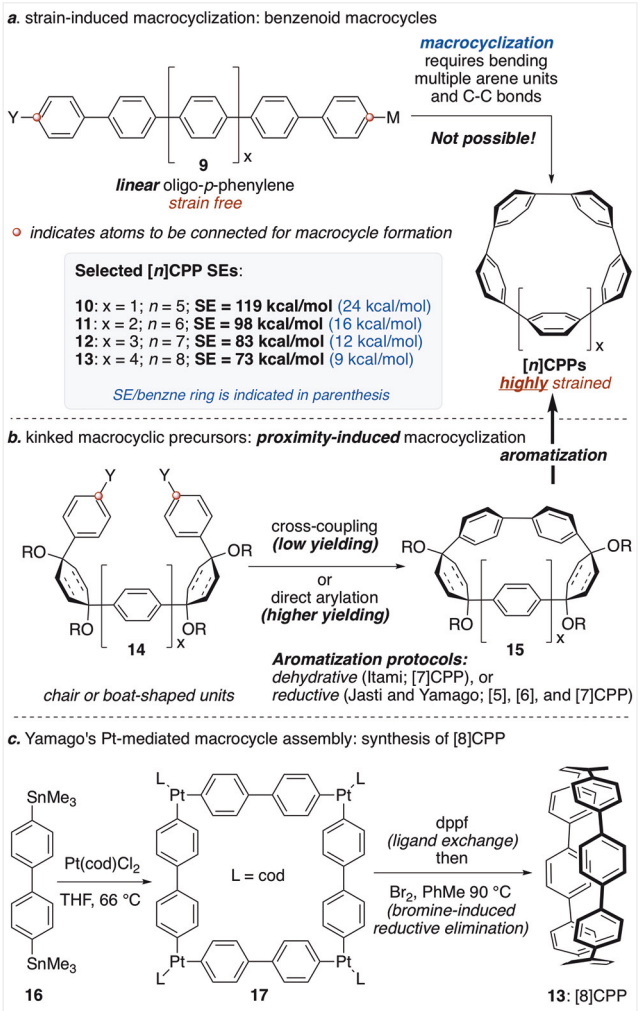
ide to aromatize the distorted cyclohexadiene ring system of **2**, the acetate esters were cleaved to furnish (±)-haouamine A (**5**). In subsequent studies,[4] Baran and co-workers utilized a dehydrogenation of bridged cyclohexenone **3** by employing a protocol developed in the Mukaiyama laboratory (Scheme 1, b).[5]



Scheme 1 Synthetic approaches to the 3-aza[7]paracyclophane core of haouamine A and B

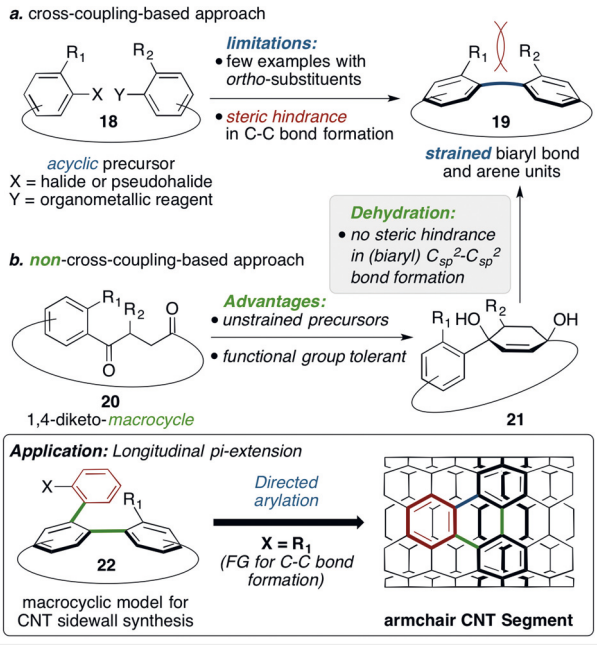
In 2012 Trauner and co-workers used the same aromatization strategy during their synthesis of the presumed structure of haouamine B, after (attempted) direct biaryl bond formation failed to produce the macrocyclic 3-aza[7]paracyclophane moiety of the marine alkaloid.[6] This work led to a structural revision of the natural product (**6**, Scheme 1, b), which was later corroborated by the Tokuyama group through a total synthesis.[7] Wipf and co-workers conducted a model study where bridged enone **7** was synthesized in 18 steps and subsequently converted into 3-aza[7]paracyclophane derivative **8** via an elimination-based aromatization protocol (Scheme 1, c).[8]

The [*n*]CPPs are macrocyclic polyphenylene systems that can be viewed as the smallest continuous benzenoid substructures of armchair carbon nanotubes (CNTs) (see Scheme 3). These designed molecules presented an enormous challenge for chemical synthesis over a 70 year period, until Jasti and Bertozzi reported the first synthesis of [*n*]CPPs in 2008.[9] The inherent strain energy (SE) of these macrocycles increases with decreasing value of *n* (Scheme 2, a)[10] and can be appreciated when one considers connecting the *para* vertices of an oligo-*p*-phenylene unit (**9**, Scheme 2, a). The latter is an impossible bond-forming process, at least at reasonable temperature and pressure. Successful syntheses of [*n*]CPPs have been reported by several research groups around the world and these have been accomplished by overcoming challenging macrocyclization reactions and the development of powerful aromatization protocols of bent pre-arene subunits.[11] The placement of boat-[12] or chair-shaped[13] pre-arene units in acyclic precursors such as **14** (Scheme 2, b) brings reacting arene vertices within proximity for C–C bond and macrocycle formation. The use of platinum-based, square-type macrocycles was



Scheme 2 Macrocyclization and aromatization strategies for the synthesis of [*n*]CPPs

skillfully employed by Yamago and co-workers in the first synthesis of [8]CPP (Scheme 2, c)[14] and subsequently in the synthesis of a series of homologues.[10a] While cross-coupling reactions were successfully employed during the macrocyclization phase of early [*n*]CPP syntheses, low chemical yields were obtained.[15] Recent advances in direct, non-cross-coupling-based arylation protocols has enabled the synthesis of increasingly strained (macrocyclic) aromatic systems,[16] however, this strategy is still at the mercy of competing intermolecular reactions during macrocyclization.[17] This problem becomes even more pronounced as steric congestion about the site of C–C bond formation is increased, or when offsite halide or pseudohalide substituents are present about the arene units to be linked (Scheme 3, a). Thus, a synthetic strategy that facilitates the formation of strained biaryl bonds that is tolerable to strategically placed functional groups (halide or pseudohalide) for future synthetic manipulations would provide an opportunity for late-stage π-extension of benzenoid systems into polycyclic aromatic hydrocarbons (PAHs; application, Scheme 3, b). Nonplanar π-systems of this sort are well-known,[18] however, their synthesis has not featured late-stage C–C bond-forming reactions that induce curvature.[19] Such reactions would require annulations on pre-existing bent arenes,[20] which represents a strategy for building sidewall segments of CNTs from macrocyclic templates such as the [*n*]CPPs. This bottom-up synthetic approach to CNTs and higher-order nanostructures has captured the attention of many research groups over the past nine years, including ours.

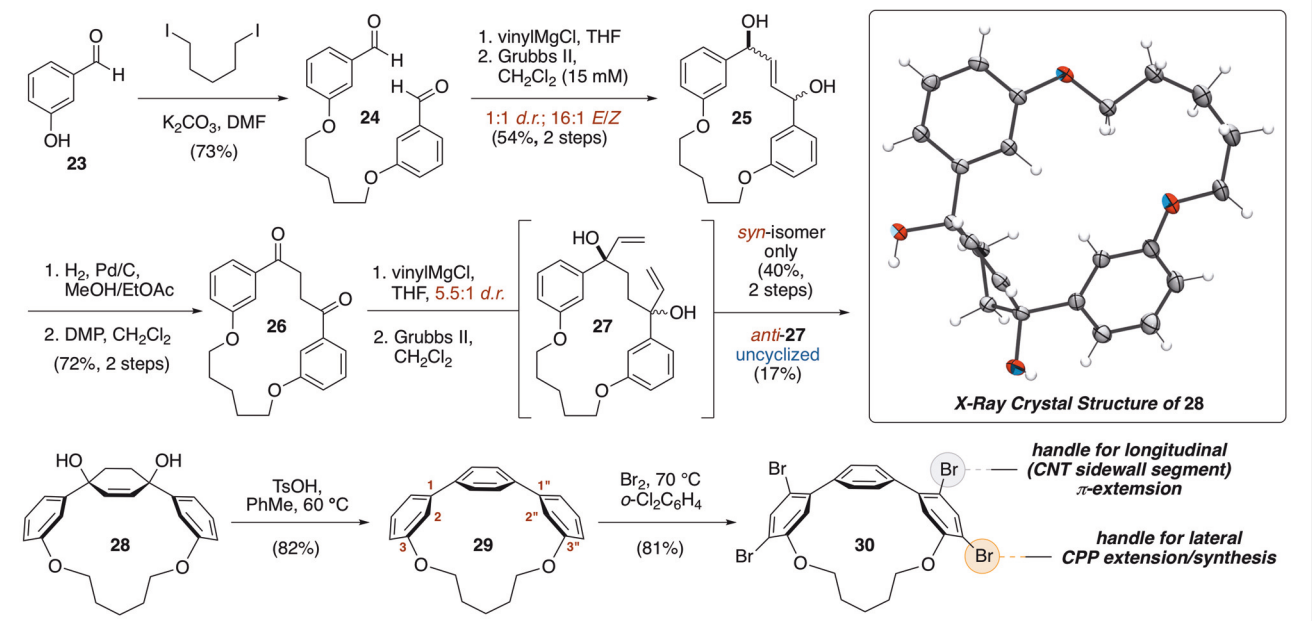


Scheme 3 Macrocyclic 1,4-diketones as intermediates to sterically hindered biaryl systems, strained *para*-phenylene rings, and models for longitudinal π-extension

To overcome the low functional-group tolerance and steric hindrance that impede cross-coupling-based macrocyclization protocols, we envisioned the use of macrocyclic 1,4-diketones in the construction of strained 1,4-arene-bridged (*para*-phenylene) units (Scheme 3, b). The carbonyl groups of the 1,4-diketo-bridging unit would ultimately take the form of the *para*-carbon atoms in the bent benzene rings.[21] As such, there is no steric requirement associated with biaryl bond formation (see **20** to **19**, Scheme 3, b). In principle, halide substituents could be selectively placed about the bridged arenes (R^1 and R^2, Scheme 3) and carried through a synthetic sequence without incident. These substituents would serve as spectator functional groups during the macrocyclization phase of the synthesis, which could be called upon at a later stage to achieve the desired skeletal building reactions. Ultimately, this type of strategy could be employed in two-directional (lateral and longitudinal) nanoscale synthesis.

2 A Non-Cross-Coupling-Based Approach to Arene-Bridged Macrocycles

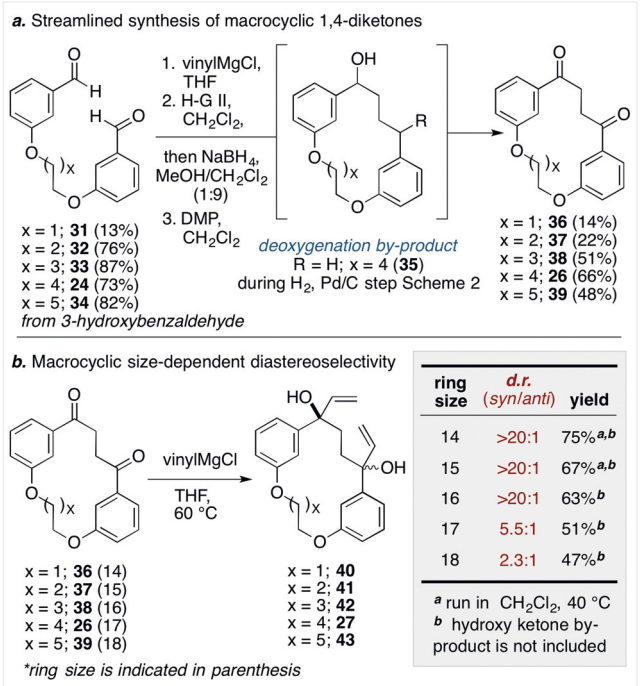
In 2015, we reported the synthesis of 1,7-dioxa[7](3,3″)*p*-terphenylophane (**29**, Scheme 4).[21] The synthesis commenced with the alkylation of 3-hydroxybenzaldhyde (**23**) to afford dialdehyde **24**. After a Grignard reaction with vinylmagnesium chloride, the intermediate allylic diol was subjected to a macrocyclic ring-closing metathesis (RCM) reaction to afford [7.4]metacyclophane **25** as a mixture of isomers. The ratio of alcohol diastereomers was determined to be 1:1 (*syn*/*anti*) upon catalytic hydrogenation of **25**, while the ratio of olefin diastereomers was determined to be 16:1 (*E*/*Z*), after direct oxidation of **25**.[21]Applying both of these steps sequentially furnished macrocyclic 1,4-diketone **26** in 72% overall yield. Treatment of **26** with vinylmagnesium chloride gave a 5.5:1 (*syn*/*anti*) mixture of alcohols that could not be separated by chromatography. Fortunately, only *syn*-**27** undergoes cyclohexene formation when subjected to a RCM reaction, and uncyclized *anti*-**27** was easily separated at this juncture. The relative configuration of **28** was corroborated by single-crystal X-ray diffraction (Scheme 4). Exposure of **28** to TsOH in toluene at 60 °C gave the target macrocycle **29** via a dehydrative aromatization reaction. The introduction of an alkyloxy chain at the 3- and 3″-positions of the *p*-terphenyl core of **29** was done with the intention to bend the teraryl system, primarily the central *para*-phenylene, and to facilitate the selective, late-stage functionalization of **29**. Indeed treatment of **29** with bromine at 70 °C gave only the tetrabromide **30** in 81% yield. It is noteworthy that the 2- and 2″-positions of the *p*-terphenyl ring system are not susceptible to bromination, as well as the central *para*-phenylene ring. In the case of the former, steric hindrance can be attributed to the attenuated reactivity, and in the case of the latter it is encour-



Scheme 4 Synthesis of 1,7-dioxa[7](3,3")*p*-terphenylophanes (**29**) using a non-cross-coupling-based strategy – first-generation approach

aging that no strain-relief-driven processes are observed under these conditions. Thus, the incorporation of electron-rich arene units in CPPs should permit the regioselective substitution of carbon nanohoops and related systems.

In order to explore the late-stage functionalization of the bent *p*-terphenyl system, the proposed two-directional skeletal building of the nanotube substructure into laterally (CPP) and longitudinally (CNT sidewalls) π-extended segments, as well as the general utility of cyclohex-2-ene-1,4-diols as precursors to bent *para*-phenylenes, a synthetic process for the gram-scale production of **26** and related homologues was pursued. During the initial scale-up phase it was discovered that catalytic hydrogenation of macrocyclic olefin **25** produced a significant amount of deoxygenated byproduct **35** (Scheme 5, a). While **35** could be easily separated from the desired reduction product, a chromatographic separation was required. Furthermore, one of the primary innovations of this non-cross-coupling-based approach to arene-bridged macrocycles was the incorporation of halide substituents in the starting aldehydes. By design, these valuable synthetic handles would not participate in competing intermolecular process during macrocyclization due to the absence of cross-coupling reactions, however, they may be susceptible to hydrogenolysis reactions under the conditions of catalytic hydrogenation. It has recently been reported that sequential RCM and transfer hydrogenation reactions can be achieved using the Hoveyda–Grubbs second-generation catalyst, and that functional groups such as benzyl ethers are tolerant of these conditions.[22] With this in mind, a modified macrocyclic 1,4-diketone synthesis was pursued.



Scheme 5 (a) Streamlined macrocyclic 1,4-diketone synthesis; (b) size-dependent diastereoselective Grignard reaction

3 Macrocyclic 1,4-Diketones: Streamlined Synthesis and Size-Dependent Diastereoselective Grignard Reactions

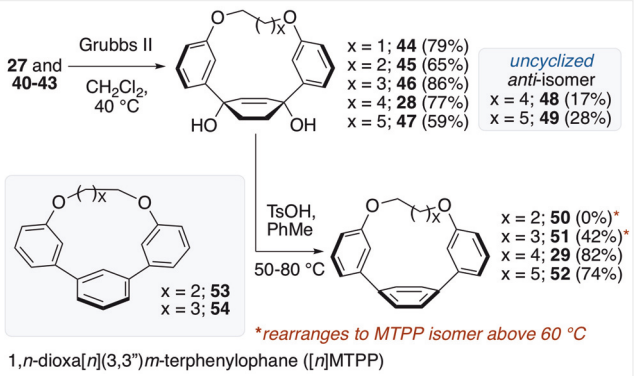
By employing a transfer-hydrogenation reaction after the macrocyclic RCM stage in the synthesis of **25**, we were able to develop a streamlined synthetic approach to a homologous series of macrocyclic 1,4-diketones (Scheme 5, a). Dialdehydes **24** and **31**–**34** can be synthesized on a gram-scale, and subjected to a Grignard reaction with vinylmagnesium chloride. After workup, the residue is taken up into dichloromethane (15 mM) and treated with 2.5 mol% of the Hoveyda–Grubbs second-generation (H–G II) catalyst. Upon completion of the RCM reaction, the solvent is evaporated to approximately 100 mM concentration, methanol (10% of the total volume), and 3.0–5.0 equivalents of sodium borohydride are added. No additional H–G II catalyst is required for the transfer hydrogenation to go to completion in under two hours. After workup, the crude mixture is subjected to an oxidation reaction with the Dess–Martin reagent.[23] At this stage, 0.2–1.5 g quantities of pure macrocyclic 1,4-diketones can be isolated after flash chromatography. In the case of smaller [*n*.4]metacyclophanes (**36** and **37**, *n* = 4 and 5, respectively), lower isolated yields were obtained (Scheme 5, a). The majority of product losses are encountered at macrocyclic RCM stage in the streamlined sequence. A significant amount of a higher molecular weight (metathesis then RCM) byproduct is accompanied by the formation of the desired macrocyclic targets.

During the synthesis of **27** a 5.5:1 ratio (*syn*/*anti*) of diastereomeric alcohols was afforded, upon treatment of **26** with vinylmagnesium chloride in THF (Scheme 4). With a homologous series of macrocyclic 1,4-diketones in hand, we noticed that higher diastereoselectivity (>20:1 d.r.) was obtained when a smaller macrocyclic ring (**38**, 16-membered ring, Scheme 5, b) was employed in an analogous Grignard reaction and lower diastereoselectivity (2.3:1 d.r.) was observed when a larger macrocyclic ring was used (**39**, 18-membered ring, Scheme 5, b).[24] Indeed, when 14- and 15-membered (rings) macrocyclic 1,4-diketones were subjected to vinylmagnesium chloride the desired *syn*-allylic diols **40** and **41** were isolated as single diastereomers. It should be noted that the Grignard reactions of **36** and **37** were run in dichloromethane and not THF. Surprisingly, higher chemical yields and less of the monoreacted (hydroxy ketone) byproducts were afforded when dichloromethane was used in place of THF. We are currently conducting a detailed investigation on the origin of diastereoselectivity in these and related macrocyclic 1,4-diketones. Larger and smaller macrocyclic systems are being investigated as well as different bridging motifs. The results of this work will be reported in due course.

4 Dehydrative Aromatization Reactions: A Powerful Tool for Synthesizing Highly Strained *para*-Phenylene Units

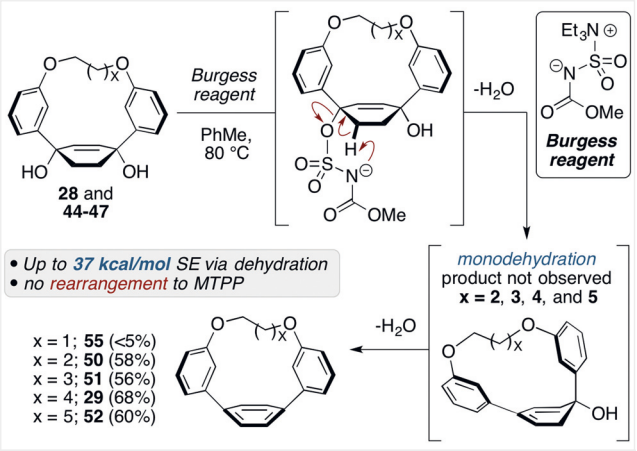
The high levels of diastereoselectivity obtained in smaller macrocyclic systems (**40**–**42**, Scheme 5, b) led to the production of greater amounts of cyclohex-2-ene-1,4-diol-based macrocycles **44**–**46**, and a simpler synthetic approach to these arene precursors (Scheme 6). In the case of **27** and **43**, the uncyclized *anti*-diastereomers **48** and **49** had to be separated via column chromatography after the mixture of allylic diols was subjected to a RCM reaction with the Grubbs second-generation catalyst (Scheme 6). With >20:1 d.r. obtained in the syntheses of **40**–**42**, nothing more than a short pad of silica gel was required to isolate pure macrocycles **44**–**46** after RCM. Applying the dehydrative aromatization reaction conditions that were used in the first-generation synthesis of **29** (Scheme 4) to a larger homologue **47**, led to the formation of the desired *p*-terphenylophane **52** in comparable yield (cf. 74% to 82%). When a smaller homologue **46** was subjected to identical protic acid conditions, a lower yield of the macrocycle **51** was obtained. Increasing the temperature of this reaction from 60 °C to 70 °C led to the formation of the less strained *m*-terphenyl isomer **54**, via 1,2-aryl migration.[24] A control experiment where pure **51** was re-subjected to TsOH in toluene at elevated temperatures (70–80 °C) supports this strain-relief-driven process from **51** and not formation of the *m*-terphenylophane from macrocyclic diol **46**. Indeed, treatment of a smaller macrocyclic system **45** with TsOH led only to the formation of **53**. The desired *p*-terphenyl derivative was observed by TLC analysis of the reaction (vide infra), however, complete conversion of the starting material into the aromatized products required increased temperatures, resulting in the rearrangement of **50** to **53**. [24]

To overcome the strain-induced rearrangement reactions of **50** and **51**, which contain increasingly distorted *para*-phenylene units, and to demonstrate the utility of our



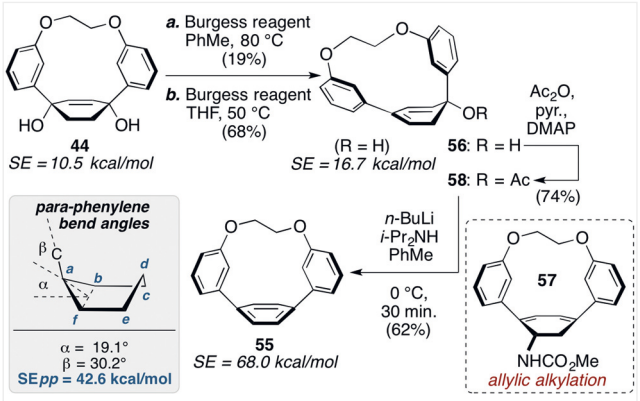
Scheme 6 Protic acid-mediated dehydrative aromatization and strain-relief-driven rearrangement of [*n*]PTPPs to [*n*]MTPPs

approach to CNT substructure synthesis, an alternative dehydration protocol was explored. The zwitterionic Burgess reagent,[25] which contains a built-in leaving group (triethylamine) for alcohol activation and internal sulfamidate-type base (Scheme 7), seemed ideally suited for this purpose. Treatment of **28** and **45**–**47** with the Burgess reagent in toluene at 80 °C gave the desired 1,*n*-dioxa[*n*](3,3″)*p*-terphenylophanes **29** and **50**–**52** (*n* = 7, 5, 6, and 8, respectively) in less than 15 minutes without the formation of the rearranged *m*-terphenyl isomers. In the case of **50**, this dehydrative aromatization protocol was capable of introducing 37.0 kcal/mol of SE in its macrocyclic framework, 28.4 kcal/mol of which is contained within the central *para*-phenylene ring.[24] This *para*-phenylene ring, which is part of a teraryl system, is slightly more strained than a monomer *para*-phenylene unit of the most strained CPP, [5]CPP, to be prepared by chemical synthesis – cf., 23.8 kcal/mol per benzene ring (see SEs, Scheme 1, a).



Scheme 7 A mild dehydrative aromatization reaction using the Burgess reagent

The success of the Burgess reagent mediated dehydrative aromatization reaction led us to investigate its application in the synthesis of an increasingly strained homologue **55**. Density functional theory (DFT) calculations, using the B3LYP functional and 6-31G(d) basis set, indicated that the *para*-phenylene ring of **55** contained 42.6 kcal/mol of SE. Furthermore, over 57 kcal/mol of SE would have to be introduced upon elimination of two molecules of water from **44**. Applying the same reaction conditions in toluene, afforded only a trace amount (<5%, Scheme 7) of the desired *p*-terphenyl macrocycle and 19% of a monodehydration product **56** (Scheme 8).[26] It is noteworthy that no monodehydration product was observed during the aromatization of **28**, and **45**–**47** (Scheme 7). If desired, the monodehydrated product of **45** could be synthesized using tin(II) chloride dihydrate in THF/toluene at 70 °C.[16a] This compound was prepared and isolated to validate the absence of its formation during the Burgess reagent mediated aromatization of **45**.



Scheme 8 Synthesis of highly strained macrocycle **55**, using iterative dehydrative reactions

Treatment of **44** (SE = 10.5 kcal/mol) with 2.0 equivalents of the Burgess reagent in THF at 50–60 °C gave **56** in 68% yield (Scheme 8). Increasing the amount of Burgess reagent used to 3.0 equivalents, led to the formation of an allylic alkylation product **57** and **56** in 31% and 42% yield, respectively, and only **57** (37%) when 4.0 equivalents of Burgess reagent was employed.[26] Signaling the limit of this dehydrative aromatization strategy, we pursued an alternative elimination-based approach. Acetylation of the tertiary hydroxyl group in **56** furnished **58** in 74% yield, which upon treatment with LDA in toluene at 0 °C afforded the highly distorted *para*-phenylene system of **55** in 62% yield via the elimination of AcOH. This reaction is capable of introducing the remaining 51.3 kcal/mol of SE into the macrocyclic structure of **44**, which, per arene unit generated, is greater than the SE induced in the Jasti and Yamago syntheses of [5]CPP – cf. 43.5 kcal/mol per benzene ring generated.

Approximately 63% of the SE for **55** is contained within the central *para*-phenylene ring, and at 42.6 kcal/mol, it exceeds that of a monomer (benzene) unit of [4]CPP – cf. 36 kcal/mol per *para*-phenylene ring (Figure 1).[10a] Combined with the biaryl units that flank the central benzene ring of **55**, this highly strained *para*-phenylene system can be viewed as model of a monomer unit of [4]CPP (**59**, Figure 1). As such, the iterative elimination protocol described in Scheme 8 would represent a suitable endgame strategy for aromatizing a precursor macrocycle of the yet to be synthesized carbon nanohoop. Whether or not such a highly strained *para*-phenylene ring will prefer a benzenoid (**59**) or quinoidal (**60**) structure has been an open question.[27] We feel that the synthesis of **55**, coupled with spectroscopic data that supports an aromatic *para*-phenylene ring (Figure 1), is suggestive that a benzenoid structure of [4]CPP is plausible. At minimum, a benzene ring containing the same biaryl bonding arrangement as a monomer unit of [4]CPP, with greater SE, can be achieved synthetically.

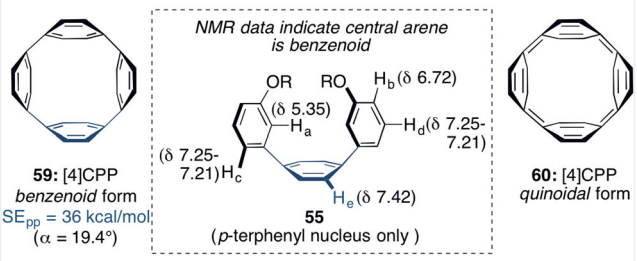


Figure 1 *p*-Terphenyl core and ^{1}H NMR chemical shifts of **55** and structures of [4]CPP.

5 Conclusion

In conclusion, the use of macrocyclic 1,4-diketones as surrogates to highly strained *para*-phenylene systems represents a non-cross-coupling-based approach to polyaryl-based macrocycles. The absence of palladium- or nickel-mediated cross-coupling or directed arylation reactions can allow for the introduction of functional group handles, such as aryl halides, at an early stage in the synthesis of more complex macrocyclic systems. Ultimately, these functional groups can remain dormant until called upon at a later stage in the synthesis of extended aromatic systems. Finally, dehydrative aromatization protocols capable of introducing up to 51 kcal/mol of strain energy in the generation of a single arene unit have been developed. The application of both of these strategies towards the synthesis of [4]CPP, π-extended macrocyclic systems, and strained arene-bridged natural products are underway in our laboratory.

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